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ARTHUR C. FORSYTH
JOSEPH R. SMITH
DAVID S. DOWNS
HARRY D. FAIR, JR.

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The Effects of Long Term Storage On Special Purpose Lead Azide

by

Arthur C. Forsyth
Joseph R. Smith
David S. Downs
Harry D. Fair, Jr.

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Explosives Division
Feltman Research Laboratory
Picatinny Arsenal
Dover, N. J.

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FOREWORD

The Explosives Division, in cooperation with the Picatinny Arsenal Spontaneous Detonation Committee, has been conducting a surveillance study of special purpose lead azide in storage. Some of the results of this work have been presented previously in internal reports to the Spontaneous Detonation Committee. This report and its appendices present the rationale for the study, the results to date, and recommendations for further work.

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ABSTRACT

Data obtained by the Explosives Division, FRL, Picatinny Arsenal, in the course of a surveillance study of stored special purpose lead azide, are presented. Two separate investigations are being reported: (1) a completed temperature cycle study; and (2) a continuing surveillance program that is concerned with the condition of the stored special purpose lead azide, and the storage containers. Included in the report are results of mechanical sensitivity tests, differential thermal analyses, microscopic surveys, and assay analyses. Relevant trip reports and laboratory studies are included as appendices.

INTRODUCTION

In recent years, large quantities of special purpose lead azide (SPLA) have been stored at Army depots, due mainly to an unanticipated reduction in the utilization of this primary explosive. Traditionally, lead azide has been manufactured and used in rather small quantities, and, as a consequence, experience relevant to the storage of large amounts for extended periods of time is virtually nonexistant. In specific instances (Ref. 1) where lead azide has been stored for long periods of time, no significant change in sensitivity to impact or thermal initiation was detected when compared with freshly prepared lead azide. However, it is well established (Ref. 2,3) that lead azide, during storage in an aqueous medium, can undergo reactions to form basic lead azide and lead carbonate. It has been suggested that the sensitivity characteristics of stored lead azide may be affected by these reaction products. Since it has been standard practice to store military grades of lead azide in a 50/50 water ethyl alcohol medium, the storage of large quantities (approximately 500,000 lb at the start of this study) becomes a matter of great concern.

It has been observed that lead azide is capable of spontaneous detonation during the processes of precipitation and crystallization. Although not completely understood, this phenomenon has been observed by numerous investigators (Ref. 4,5), and several hypotheses have been proposed to explain its occurrence.

Serious consideration, consequently, must be given to the possibility of recrystallization from the storage medium, since future storage times are predicted to be of long duration, and the storage conditions portend cyclic temperature changes conducive to recrystallation because of the slight lead azide solubility in the storage medium.

This report presents data obtained by the Explosives Division during a surveillance study of stored SPLA. Two separate investigations are reported: (1) a completed temperature cycle study; and (2) a continuing surveillance program that is concerned not only with the condition of the SPLA, but also with the condition of the storage containers.

EXPERIMENTAL PROCEDURES

Sampling Procedures

The lead azide is stored in above-ground, dome-shaped magazines, which are covered with earth and seeded with grass. A complete description of the packaging used by the manufacturers of lead azide is given in Appendix A. In most cases (Appendix A, Fig 1-3) 15 to 25 pounds of lead azide are wrapped in a square diaper cloth and placed inside a succession of rubberized or polyethylene bags containing a 50/50 alcohol-water solution. These bags of lead azide are enclosed in a jute or canvas liner, embedded in sawdust, and placed inside a 55 gallon drum. Each drum is filled with 50/50 alcohol-water solution and contains 125 to 150 pounds of lead azide.

In the process of procuring lead azide samples from storage for this study, some deterioration of packaging materials was observed. Appendix A gives the analyses of the storage liquid at various locations within the storage drum. A description of the type of packaging deterioration encountered can be found in Appendices A through H.

Temperature Cycling Study

Twenty-six representative samples of SPLA and six of RD 1333 lead azide from the various manufacturers were selected from storage and shipped to Picatinny Arsenal in an alcohol-water mixture. The samples were not delivered to the Explosives Division in the original storage solutions; so upon arrival at the laboratory they were filtered and washed with a 50/50 alcohol-water solution, reapportioned into 25 g test quantities, and stored under a fresh 50/50 alcohol-water solution in vapor-tight[1] polyethylene bottles. The actual lead azide storage environment was simulated as closely as possible by including swatches of duck cloth, diaper cloth, and polyethylene bag material in each of the bottles. Prior to use, both types of cloth were washed repeatedly with distilled water until no trace of sizing coloration appeared in the washwater.

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[1] Prior to use, a laboratory test was conducted to verify the manufacturer's claim as to sealing qualities. Bottles containing 50/50 alcohol-water were placed in storage at 40°C for a total period of approximately 40 days and tested at 4 day intervals. Total weight loss was less than .5% for all tests of the bottles used for this study.

The samples were then placed in an unheated above-ground storage building. It was determined that the variation in temperature in this storage facility was not significantly different from that encountered in storage magazines at the Savanna and Ravenna Depots; if anything, the temperature differentials were slightly greater at the Picatinny facility. When withdrawn for tests, the samples were filtered, washed with 50/50 alcohol-water solution, and then again with acetone. Following this treatment, a portion of each sample was taken for impact testing, and another one for the micrographic and differential thermal analysis studies.

Surveillance Study

Under the supervision of a representative of the Explosives Division, the samples were withdrawn from the storage drums at the various storage locations. A sample of sufficient quantity to allow for evaluation, testing, and specimen retention, was packed in storage medium taken from the same drum, placed in a suitable container, and shipped to Picatinny Arsenal. Surveillance reports assessing the condition of the storage containers and internal packaging materials are given in Appendices C through H. After arrival at Picatinny Arsenal, the samples were stored in the original medium until just prior to testing, at which time they were filtered and washed with 50/50 alcohol-water solution followed by a thorough acetone wash.

Mechanical Sensitivity Test Procedures

In the course of these investigations the use of the so-called ball drop impact apparatus was substituted for the PA impact apparatus to evaluate samples as to their mechanical sensitivity. The changeover was made primarily to take advantage of the much lower cost of the ball drop procedure. Since, however, absolute values of impact sensitivity data (e.g., 50% firing heights) are not comparable for the two cases, the changeover was made only after a sufficient number of runs had been made to establish confidence in the reliability of the ball drop test. The first step in the evaluation of that test consisted of subjecting ten batches of one lot of RD 1333 lead azide to ball drop initiation (see Appendix J). The results show excellent reproducibility of the 50% heights, but the standard deviations obtained are generally larger than those obtained in PA impact tests of lead azide. To supplement that test, the first group of surveillance samples were subjected to both PA impact and ball drop impact The results are tabulated in Table 3. Although the standard deviation is greater, the relative variation (standard deviation as percent of mean value) is smaller for the ball drop test, indicating that it is a more precise procedure than the PA impact test (see Appendix K).

Both types of test apparatus are located in a temperature and humidity controlled room to minimize environmental effects. The samples were placed in this environment for one hour prior to testing.

Since the results of these tests are notorious for their dependence upon non-sample-dependent parameters, particular care was taken to minimize the effects of extrinsic factors by (1) fabricating all metal parts of the test fixtures at one time from common stock, (2) employing the same closely supervised test operator and loader throughout the series of tests, and (3) maintaining a well controlled loading and firing sequence. To continually verify the reproducibility of the impact apparatus, a "monitor" sample was tested at intervals during the test sequence. This sample was stored in a desiccator, and one hour prior to testing, the required amount was removed and left in the room environment for one hour, as were the test samples.

Picatinny Arsenal Impact Test

Impact test parts were manufactured in large quantities, and representative parts were selected, loaded with the "monitor" and test fired. The results of these tests, when compared with other "monitor" test results served as a criterion for assuming the acceptability of PA impact test parts. All the test fixtures for each sample, at each test period, were loaded consecutively. There were 180 fixtures, 140 for the test sequence and 40 for recheck purposes.

Twenty shots were fired at each test height; the heights were changed in one inch increments, and a sufficient number of heights was tested to give a percentage fire record extending from 10% to 90% fire. The additional 40 samples were used to verify the 50% height and one differing height selected at random.

DuPont Ball Drop Test

The samples were prepared for testing in manner identical to that discussed in the preceding section "Surveillance Study". Twenty drops were made at each reported drop height, and at least five heights were tested for each sample.

Differential Thermal Analysis Procedures (DTA)

Thermal analysis has been suggested as a technique for the characterization of the sensitivity of explosives (Ref 6,7). The thermal decomposition of lead azide may proceed by the reaction

$$PbN_6 \rightarrow Pb + 3N_2 \text{ gas}$$

or, as is more probably the case in the presence of small amounts of oxygen,

$$PbN_6 + \text{trace } O_2 \rightarrow PbO + 3\,N_2 + \text{higher oxides of Pb.}$$

Without special precautions, the latter is the reaction most commonly observed in DTA analyses, and yields an ill-defined product consisting of a variable mixture of metal plus oxides, with no assurance that the same reaction products will be obtained in any two experiments.

A DuPont 900 DTA has been modified to permit the complete exothermic decomposition of lead azide to be observed. This modification and the suggested experimental procedure (Ref 7) provide a technique for obtaining complete reproducible decomposition curves of lead azide without the complications concomitant with the formation of intermediate reaction products.

Microscopic Survey and Photomicrographic Procedures

A typical microscopic survey consists of a thorough examination of at least five microscope slides prepared from random areas of a bulk sample. In the procedure referred to in this report, a small amount of water-damp lead azide was placed on a glass slide, and acetone was added to disperse and dry the particles. The slides were thoroughly examined for the presence of newly formed crystals. Also, any agglomerates or crystals of unusual size and shape were noted and recorded. The five slides were examined, a representative slide selected, and photomicrographs taken of at least two areas of the slide, as well as of any unusual particles found during the examination. The photomicrographs were indexed and retained as permanent records.

Assay (% PbN_6) Analysis Procedures

A colorimetric procedure (Ref 8) was used to determine the azide ion content of the sample. The percent lead azide present was calculated from these results.

RESULTS AND DISCUSSION

Temperature Cycling Study

Representative samples of SPLA and RD 1333 lead azide were tested at approximately three month intervals, corresponding to the seasonal variations; in this report they are denoted as the first, second, and third cycle respectively. Concurrent with the SPLA study, several RD 1333 samples were tested for comparison.

The main objective of this portion of the study was to determine the effect of seasonal temperature variations on the mechanical sensitivity of lead azide, and to assess whether there is any periodic recrystallization from the storage medium.

Mechanical Sensitivity (Impact Testing)

Since there has been no absolute measure of sensitivity (and hence, of hazard), the essential function of an impact test is to provide a relative listing, ordering, and grading of the mechanical or impact sensitivities of a group of samples. Freshly manufactured SPLA should be used as the standard or basis for assessing any changes in properties due to storage. Unfortunately, impact data for freshly prepared production SPLA were not available, and SPLA was no longer in production at the start of this investigation, thus preventing the collection of such data.

In order to establish an appropriate basis, impact sensitivity curves were obtained for 26 samples "as received" from storage. These data, when plotted together, define an envelope of drop height and percent fire values, which has been used as the basis for comparison of subsequent impact sensitivity data. Thus, one criterion for establishing a change in impact sensitivity due to storage is the observation of drop height data lying outside this envelope. Unfortunately, the associated degree of hazard is a matter of judgment and experience.

The raw impact data consist of the number of "fires" and "no fires" at each drop height. Sensitivity curves are obtained by plotting, on probability scale graph paper, the least squares fit of the drop height data in inches, as a function of percent fires. The impact curves represent the sensitivity most accurately between the 10% - 90% initiation points. Obviously, the major interest with respect to hazards occurring due to increased impact sensitivity is at the very small percent initiation level.

Of the initial 26 special purpose lead azide samples, six were

selected at random for the temperature cycle study. The impact curves for these samples are given in Fig 1 through 6 for the "as received" and first three cycles data. Superimposed on these data is the envelope of the sensitivity curves for the initial 26 SPLA samples, to indicate, not only any changes of the individual sample, but also its sensitivity in relation to the SPLA basis as described above. A summary of the sensitivity values (10% and 50% heights) calculated from a least squares analysis of the data points appears in Table 1.

The t-distribution functions for these data are used in order to calculate the probability of distinction between any two samples. This probability is obtained directly from an estimate of the overlap of the t-distribution functions for two samples. For example, $P_{distinct}$ = 95% means that the distributions are well separated, and there is a high probability that the two samples have significantly different sensitivities to impact. Conversely, a low probability of distinction implies that no significant difference in impact sensitivity has been established. Table 2 shows the probability of distinction values for the three cycles if compared with the corresponding "as received" data.

In summary, two methods of evaluating changes of mechanical sensitivity are used. If the sensitivity plot of a set of data falls outside the standard envelope, and/or if the calculated probability of distinction between data on any sample and its corresponding "as received" data is large, it is assumed that the impact sensitivity of the sample has undergone sufficient change to warrant concern and further investigation.

The data presented in Tables 1 and 2 and Fig 1 through 6 indicate no significant change of impact sensitivity for the SPLA samples studied.

It can be seen from Table 2 that in general the samples with initially high probabilities of distinction become less distinct in successive cycles, and those with low probabilities at the outset become more distinct. An observation which may be relevant in this context is that samples which show decreasing probability of distinction are white, while those exhibiting an increase tend to be colored.

In all cases but one, the second cycle showed the highest probability of distinction when compared with the "as received" results. What importance, if any, can be placed on the sequence of change in the probability of distinction values is not apparent. It must suffice to say that it may be related to impurity content, which in turn can depend upon the care used in packaging.

There was no trend established that could have been considered

indicative of a continuing increase or decrease of mechanical sensitivity. It appears from the probability of distinction analysis, that the temperature just prior to sampling for measurement is more important in influencing the apparent sensitivity than any thermal cycling effects. The impact sensitivity curves obtained for the RD 1333 samples tested exhibit the only instance where impact curves obtained for a cycle sample fell out of the envelope. Originally it was intended to test only one RD 1333 sample; but the results obtained for that sample (Fig 7) warranted testing another one (Fig 8). It can be seen from Fig 7 and 8 that the impact sensitivity curves for the cycled material, for both samples, have at least a portion outside the envelope. Consequently, it would appear that the results obtained for the RD 1333 give more reason for concern than those obtained for SPLA samples.

Differential Thermal Analyses (DTA)

DTA traces were obtained for all "as received" and first cycle samples. The DTA analyses were not continued for later cycles, since the traces for the first cycle samples were found to be almost identical to those for the "as received" samples. A representative set of DTA traces is shown in Fig 9 and 10; the peak temperatures taken from the "as received" and first cycle traces are listed in Table 2 of Appendix 9. It can be seen that in only one instance does a first cycle sample's peak temperature differ from an "as received" result by more than one degree C.

Microscopic Survey

Military specifications require that production lead azide (SPLA and RD 1333) contain no well defined crystalline material if observed through a microscope. With a few exceptions, photomicrographs taken of SPLA and RD 1333, as received from storage, show satisfactory agreement with this requirement (Fig 11). However, following each temperature cycle the photomicrographs indicate the appearance of small crystallites and, in some cases, the growth of clear crystalline material on the lead azide particles. Fig 12 and 13 demonstrate the clarity and show the well-defined crystalline faces of the crystallites. It should be emphasized, however, that the number of the crystallites is not large. (These photomicrographs were chosen specifically to indicate the nature and morphology of the crystallites and are not indicative of their concentration.)

The presence of the crystallites indicates that recrystallization can occur from a medium which is the same as that used for bulk storage. This is an important observation in light of the fact that spontaneous

detonations have occurred under certain conditions of recrystallization.

X-Ray Diffraction Study

X-ray diffraction spectra of "as received" SPLA samples, using standard techniques, show that, regardless of their noncrystalline appearance and the outer configuration of the particles, they are predominantly alpha lead azide. In order to ascertain the structure of the clear crystallites and other suspect particles, micro-focus X-ray techniques had to be employed. Standard X-ray techniques are not sufficiently sensitive to distinguish small concentrations of, say, β-lead azide in a sample composed predominantly of α-lead azide.

Of particular interest were crystallites that had an extremely elongated appearance, which suggested the possibility of their being the monoclinic or beta form of lead azide. Of course, such particles could also be a salt of carboxymethylcellulose or some foreign material. A sufficient quantity of the crystallites was physically separated from the bulk lead azide, transported to the National Bureau of Standards, and examined individually using micro-focus X-ray analysis. Photomicrographs of the type of crystals examined are shown in Fig 13. The crystals were identified as alpha lead azide. It is hypothesized that the elongation resulted from a series of time separated crystal growth periods which occurred when temperature conditions were favorable for crystallization.

Surveillance Study

Mechanical Sensitivity

The impact test results for the first and second annual surveillance studies are given in Tables 3 and 4. Also shown in these tables are the date of manufacture for each sample and the installation where each was stored at the time of sampling. Both PA impact and ball drop data are given for the first set of samples, and only ball drop data for the second set, since it was during the interim that the changeover to the ball drop test was effected. It should be noted that the cost savings realized by this substitution allowed for the impact testing of almost twice the number of samples for the second surveillance study.

Impact sensitivity plots of the ball drop data have been grouped according to manufacturer for each annual sampling and are given in Fig 14 through 17. The shaded areas superimposed on the second surveillance results (Fig 15 and 17) represent the envelope defined

by the first sampling data. Figure 14 indicates the reproducibility of the test using a standard monitor sample. Naturally, no trend of the data can be considered to be definite until at least one more sampling is done. The results obtained for E.I. DuPont samples, Fig 17, show a grouping of five samples to be above and outside the superimposed envelope. What is considered to be of significance about this result is that all of these samples were manufactured in 1967. The plots obtained for Uniroyal (JAAP) samples (Fig 15) show that all the second surveillance samples are closely grouped and fall within the envelope. In this case it appears that samples manufactured in both 1967 and 1968 have shown no apparent change in impact sensitivity.

In an attempt to relate the results obtained to various criteria, e.g., packaging configuration, storage media coloration, storage area, etc, two correlations have been found:

(1) All of the E.I. DuPont SPLA has been stored at or moved to SAD, while all of the Uniroyal (JAAP) material has been stored at JAAP. The significance of this is not obvious since both installations have the same type of storage facilities (igloos), and both follow standard surveillance procedures.

(2) A review of the trip reports presented in the Appendices shows that the principal differences of packaging configuration are the number of outer plastic bags used and the interior coating of the storage drums. The inspections reveal that the medium coloration for the DuPont package is more intense at the drum and in the second layer, but the solution in contact with the azide indicates very little permeation of the bag containing the azide. In the case of the Uniroyal packaging configuration, the color of the medium at the drum and through all layers of the packaging configuration shows little change. The medium in contact with the drum has much less coloration than that of the DuPont packages, due to the corrosion protection afforded by the phenolic coating on the inside of the drum.

The absence of color permeation into the interior DuPont bag, induces a certain temptation to hypothesize that hydrolysis products of the reaction of the lead azide with water are trapped in the inner bag of the DuPont packages. However, it remains to be shown that such entrapment favors the formation of basic lead azide, which is thought to be the cause of a decrease in mechanical sensitivity.

Photomicrographic Survey

The microscopic analyses, including photomicrographic records, have been completed for all of the first surveillance group of samples

and are under way for the second group. Of the 18 samples examined and photographed for the first surveillance group only two showed any signs of abnormality. One sample (Lot JA 4-71) contained numerous small rounded particles not seen in any of the other samples tested to date. The rounded form of the particles would indicate that they were formed during precipitation in the presence of the crystal modifier. The other sample (Lot JA 4-76) contained a large number of crystals with a spinelike growth that appears to be crystalline. In the impact sensitivity tests or assay analysis, neither of these samples exhibited any abnormalities that might indicate an undesirable situation, and both were colorless to the eye. Photomicrographs of these samples are shown in Fig 19. It was decided that the rounded particles, although abnormal, were inconsequential and should provoke no great concern. However, the possibility exists that the spinelike growths seen are the results of recrystallization, making their appearance consequential, regardless of the test results.

It was decided to hold in abbeyance any recommendations as to action to be taken pending examination of later surveillance samples. This should allow for a more complete assessment as to frequency of occurrence of these particles, and the detection of any growth of the spines.

Assay (% PbN_6 Analysis Procedures

The physical appearance (principally color) of some of the first surveillance samples raised doubts as to whether the material could meet specification requirements. Concern over this factor prompted the introduction of assay analysis into the program. It can be seen from Table 5 that many samples assay lower than required by military specification ($\leq$ 98.5%). However, it should be remembered that these samples were placed in storage between the years 1966 - 1968, and therefore no comparison can be made between these values and the purity at the time of manufacture. Furthermore, the sample exhibiting an extremely low purity value (OM 1-16) is among those destroyed for reasons of storage container deterioration. At this writing, the analysis of only ten of the second surveillance group of samples has been completed. It shows no real change of purity if compared with the first surveillance group samples.

SUMMARY AND RECOMMENDATIONS

The results of the temperature cycle studies indicate that seasonal temperature variations do affect the results of mechanical

sensitivity tests of stored SPLA, but that extremes of temperature just prior to the sampling may obscure any trends which may be present.

The impact sensitivity tests performed in the course of the surveillance study show a definite change in sensitivity of some samples over the period of one year. However, to establish a definite trend, a minimum of three annual samplings will be required.

A principal part of the surveillance study has been the careful examination of the packaging and containers. The detection of serious deterioration of Olin Mathieson containers was a major factor in the subsequent decision to destroy that material. Packaging configurations, permeability of plastic containers, and drum liner material are considered to be important factors, which will have their effects on the long term changes in sensitivity of the stored SPLA.

The continuation of surveillance studies will assure the early detection of changes in impact sensitivity of SPLA, deterioration in storage containers, and detection of any new crystalline formations and structures. In addition, it is recommended that other available sensitivity tests, e.g., electrical spark initiation and explosion temperature, be used in conjunction with impact testing. Both wet and dry samples have been retained for the purpose of such an expanded test program.

The properties of the packaging materials also have been suggested as an important factor in long term storage. It is strongly recommended that additional studies be undertaken to determine reactions occurring because of the permeability, or impermeability, of the packaging materials. Preliminary laboratory investigations (see Appendix I), using more sophisticated analytical techniques such as electron spin resonance, suggest that increases in the amount of iron or manganese present in the stored SPLA may be an indication of reactions occurring with the storage medium. These results also indicate a need for more detailed studies of the possible use of "getter" materials to inhibit undesirable reactions when materials are stored in a liquid medium.

The observation of crystalline material indicates a need for continued surveillance and a better characterization and understanding of the spontaneous detonation phenomenon. It is suggested that work of a more fundamental nature is required to determine the effects of crystalline modifiers (such as carboxymethylcellulose) and other physical parameters on the probability of spontaneous detonation during precipitation of lead azide from solution. Particular emphasis should be given to the effects of precipitating RD 1333, special purpose, and pure lead azide from the storage medium.

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TABLE I

Impact Sensitivity Test

Heights at 10% and 50% Fire

	As Received		1st Cycle		2nd Cycle		3rd Cycle	
SPLA Sample	10%	50%	10%	50%	10%	50%	10%	50%
Lot Dup 53-17	6.50	8.20	5.10	6.80	5.19	6.95	5.10	6.82
Lot Dup 53-44	6.77	9.41	4.48	7.20	5.22	7.02	5.05	7.00
Lot JA 4-52	6.39	8.66	4.78	7.45	5.13	6.61	7.60	9.70
Lot JA 4-84	6.20	9.64	6.20	8.78	5.25	7.25	6.38	7.78
Lot OM 66-25	6.29	8.37	4.89	7.61	4.81	6.78	5.27	7.23
Lot OM 67-5	3.48	6.72	3.35	5.95	4.58	6.38	5.21	6.53
Monitor	5.17	6.81	4.45	6.49	4.58	6.90	5.48	7.28
	19 Jan 70		11 Feb 70		8 May 70		9 June 70	
RD 1333 Samples								
Lot OM 2-2	6.96	8.76	3.02	5.74	4.76	6.44	3.93	6.29
Lot Dup 51-32-6	5.12	7.02	---------		---------		5.14	7.62
Dates of Cycle	3/69		3/69	17/9/69	3/69	15/1/70	3/69-23/5/70	

TABLE 2

Probability of Distinction Values

Special Purpose Lead Azide	1st Cycle vs As Received	2nd Cycle vs As Received	3rd Cycle vs As Received
Lot Dup 53-17	64%	73%	76%
Lot Dup 53-44	73%	93%	91%
Lot JA 4-52	52%	88%	62%
Lot JA 4-84	39%	86%	78%
Lot OM 66-25	30%	73%	64%
Lot OM 67-5	38%	17%	12%
Lead Azide RD 1333			
Lot OM 2-2	95%	98%	95%
Lot Dup 51-32-6	--	--	38%

TABLE 3
Impact Sensitivity Test Results for 1st Surveillance

1st Surveillance Samples

Sample	P.A. Test 50% Hgt	P.A. Test Std Dev	Ball Drop Test 50% Hgt	Ball Drop Test Std Dev	Manu-factured	Stored
OM 66-31	9.4	1.4	23.4	3.6		
OM 67-17	9.2	1.8	23.6	4.4		
OM 1-16	11.1	2.4	22.0	3.0		
OM 1-19	9.7	2.0	27.4	4.1		
OM 1-22	9.7	2.1	22.3	2.7		
OM 1-25	9.2	2.0	26.8	3.2		
DUP 53-24	9.1	2.1	23.2	3.2	67	SAD
DUP 53-36	9.9	1.8	20.9	3.0	67	SAD
DUP 53-54	10.0	1.6	22.3	2.5	67	SAD
DUP 53-72	9.9	2.0	18.4	3.3	67	SAD
DUP 53-82	9.6	1.6	22.0	3.0	68	RAAP
DUP 53-91	10.2	1.6	21.2	2.3	68	SAD
JA 4-55	9.3	1.4	24.9	1.9	67	SAD
JA 4-71	9.2	1.0	19.4	1.9	1/15/68	JAAP
JA 4-76	9.2	1.2	23.5	2.1	10/20/67	JAAP
JA 4-82	9.4	1.6	22.3	5.2	11/17/67	JAAP
JA 4-88	9.2	1.5	21.1	2.6	9/30/67	JAAP
JA 4-91	9.4	1.5	19.6	2.9	12/15/67	JAAP
Monitor Sample Tests						
	9.3	2.0	19.6	3.9		
	9.7	1.9	19.5	2.2		
	8.8	1.5				

TABLE 4

Impact Sensitivity Test Results for 2nd Surveillance

Ball Drop Test

Sample	50% Hgt	Std Dev	Manu-factured	Stored
JA 4-73	21.5	2.2	10/9/67	JAAP
JA 4-74	21.6	2.7	10/12/67	JAAP
JA 4-75	22.3	2.5	10/16/67	JAAP
JA 4-79	22.8	3.0	11/6/67	JAAP
JA 4-80	21.8	2.4	11/9/67	JAAP
JA 4-82	20.0	2.3	11/17/67	JAAP
JA 4-83	21.0	2.7	11/22/67	JAAP
JA 4-85	20.8	2.7	12/4/67	JAAP
JA 4-87	21.2	2.8	12/12/67	JAAP
JA 4-89	23.1	3.2	12/19/67	JAAP
JA 4-90	22.0	2.4	1/9/68	JAAP
JA 4-92	23.4	3.9	1/19/68	JAAP
JA 4-93	23.3	4.7	1/24/68	JAAP
JA 4-94	21.3	2.4	1/29/68	JAAP
JA 4-96	20.9	3.4	2/12/68	JAAP
JA 4-97	21.3	2.4	2/16/68	JAAP
DUP 53-18	28.3	3.0	67	SAD
DUP 53-21	26.9	2.9	67	SAD
DUP 53-23	27.1	3.8	67	SAD
DUP 53-25	27.4	3.3	67	SAD
DUP 53-32	26.6	3.9	67	SAD
DUP 53-35	22.7	3.8	67	SAD
DUP 53-38	23.6	2.9	67	SAD
DUP 53-44	23.4	2.6	67	SAD
DUP 53-51	23.3	1.8	67	SAD
DUP 53-73	22.9	2.8	67	SAD
DUP 53-75	20.6	2.5	67	SAD
DUP 53-76	21.9	2.9	68	SAD
DUP 53-77	23.2	2.8	68	SAD
DUP 53-79	21.4	2.7	68	SAD
DUP 53-91	23.0	3.0	68	SAD
DUP 53-92	21.4	3.3	68	SAD
Monitor Tests	21.2	2.4		
	20.9	2.4		

TABLE 5

Assay Analyses (%PbN_6) Results for Surveillance Study

1st Surveillance Samples			2nd Surveillance Samples*		
Sample	Color	%PbN_6	Sample	Color**	%PbN_6
OM 66-31	Buff	96.8	JA 4-73	White	97.8
OM 67-17	Pink	97.3	JA 4-74	White	97.5
OM 1-16	Grey	93.7	JA 4-75	White	97.1
OM 1-19	Pink	98.4	JA 4-79	White	97.7
OM 1-22	White	98.2	JA 4-80	White	96.9
OM 1-25	White	96.7	JA 4-83	White	98.2
DUP 53-24	White	98.9	JA 4-87	White	98.7
DUP 53-36	White	98.2	JA 4-89	White	96.6
DUP 53-54	White	97.0	JA 4-90	White	97.5
DUP 53-72	White	97.2	JA 4-94	White	97.8
DUP 53-82	White	98.4	JA 4-96	White	97.1
DUP 53-91	White	97.1	JA 4-97	White	97.2
JA 4-55	White	96.4			
JA 4-91	White	96.7			
JA 4-76	White	97.5			
JA 4-82	White	96.7			
JA 4-71	White	98.4			

*Samples analyzed at time of report of a total of 32 samples.
**All 2nd Surveillance Samples from both E.I. DuPont and Uniroyal were white.

Special Purpose Lead Azide
Lot #JA-4-84

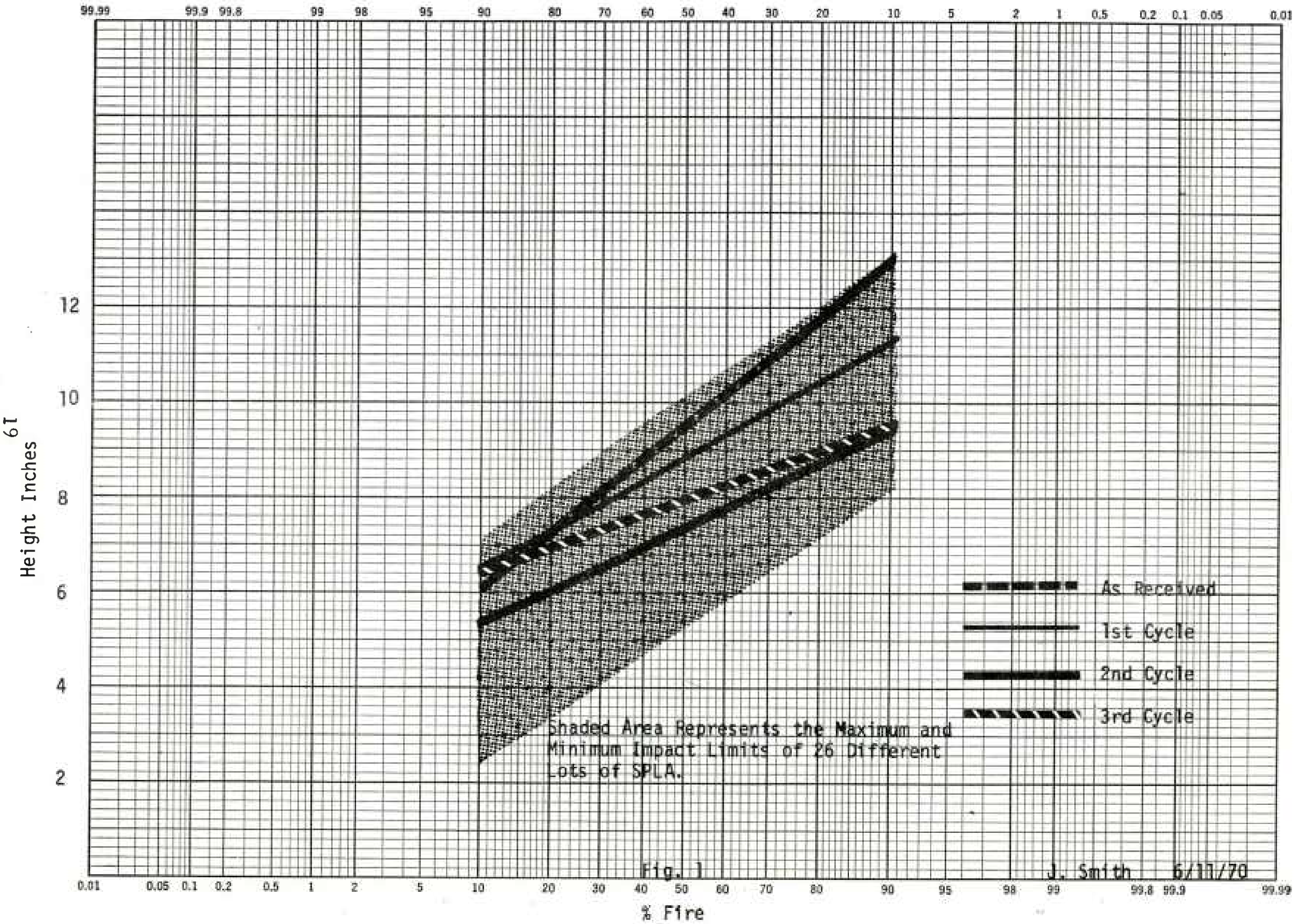


Fig. 1

Special Purpose Lead Azide
Lot #OLIN-67-5

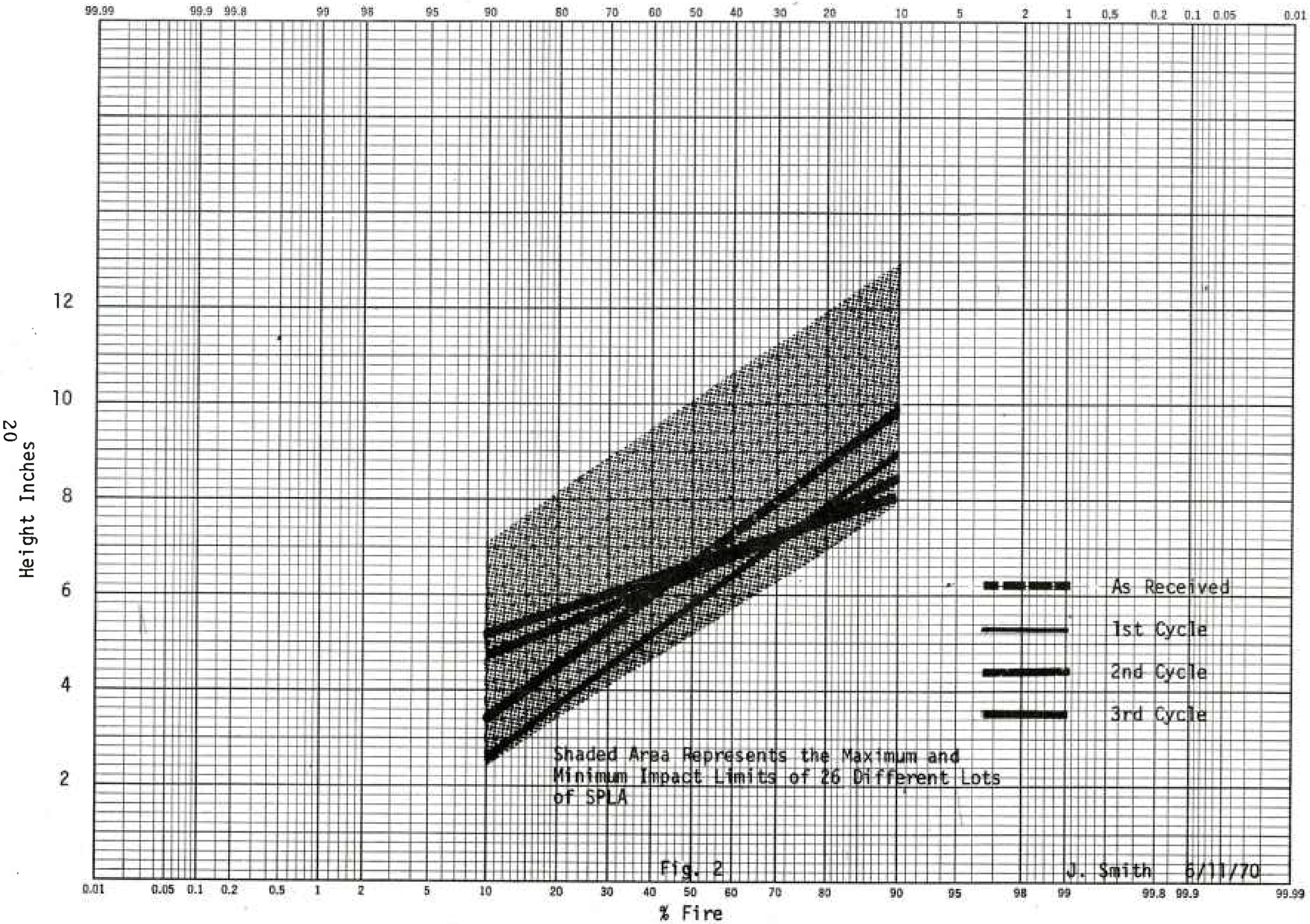


Fig. 2

Special Purpose Lead Azide
Lot #OM-66-25

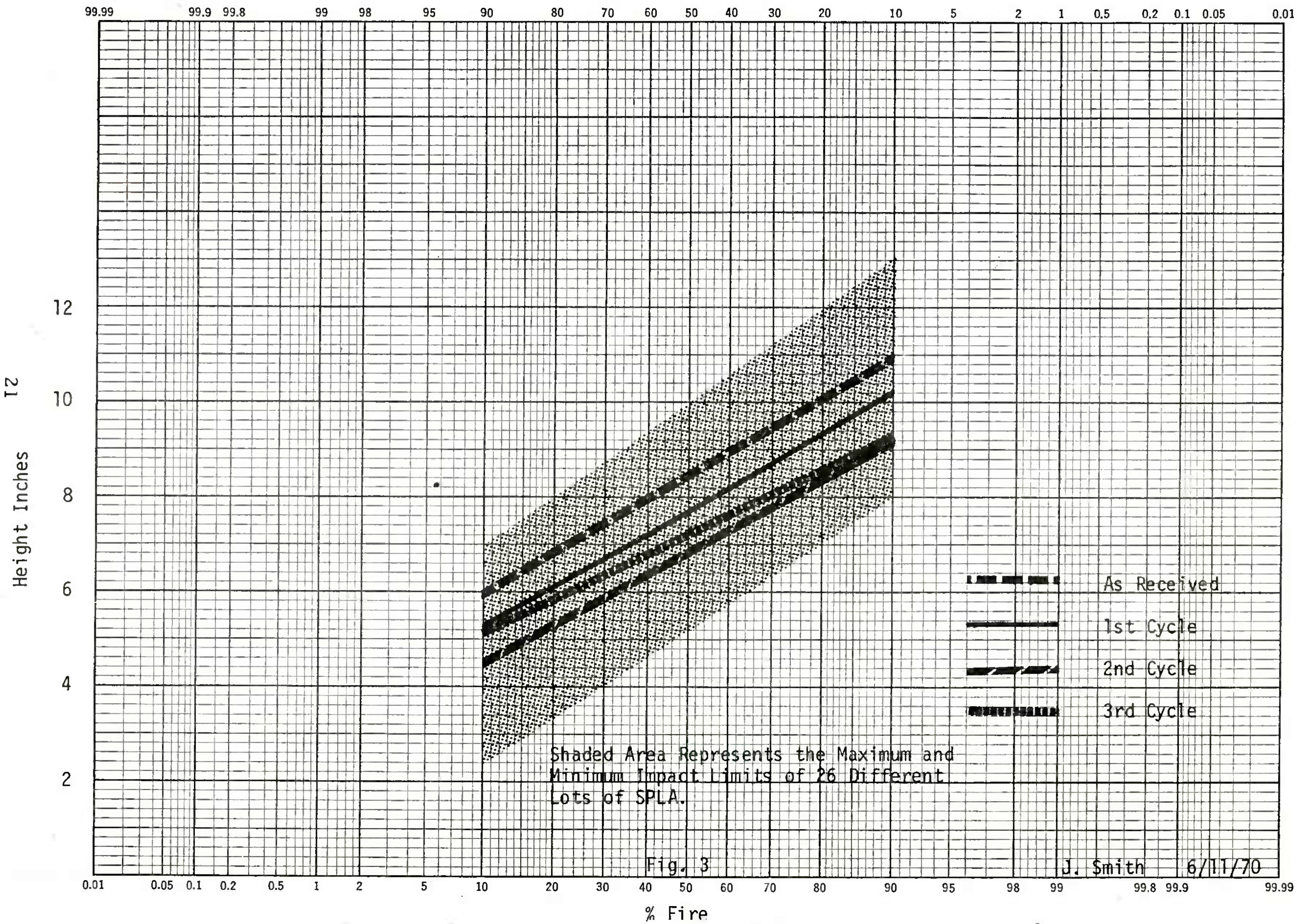


Fig. 3

Special Purpose Lead Azide
Lot #JA-4-52

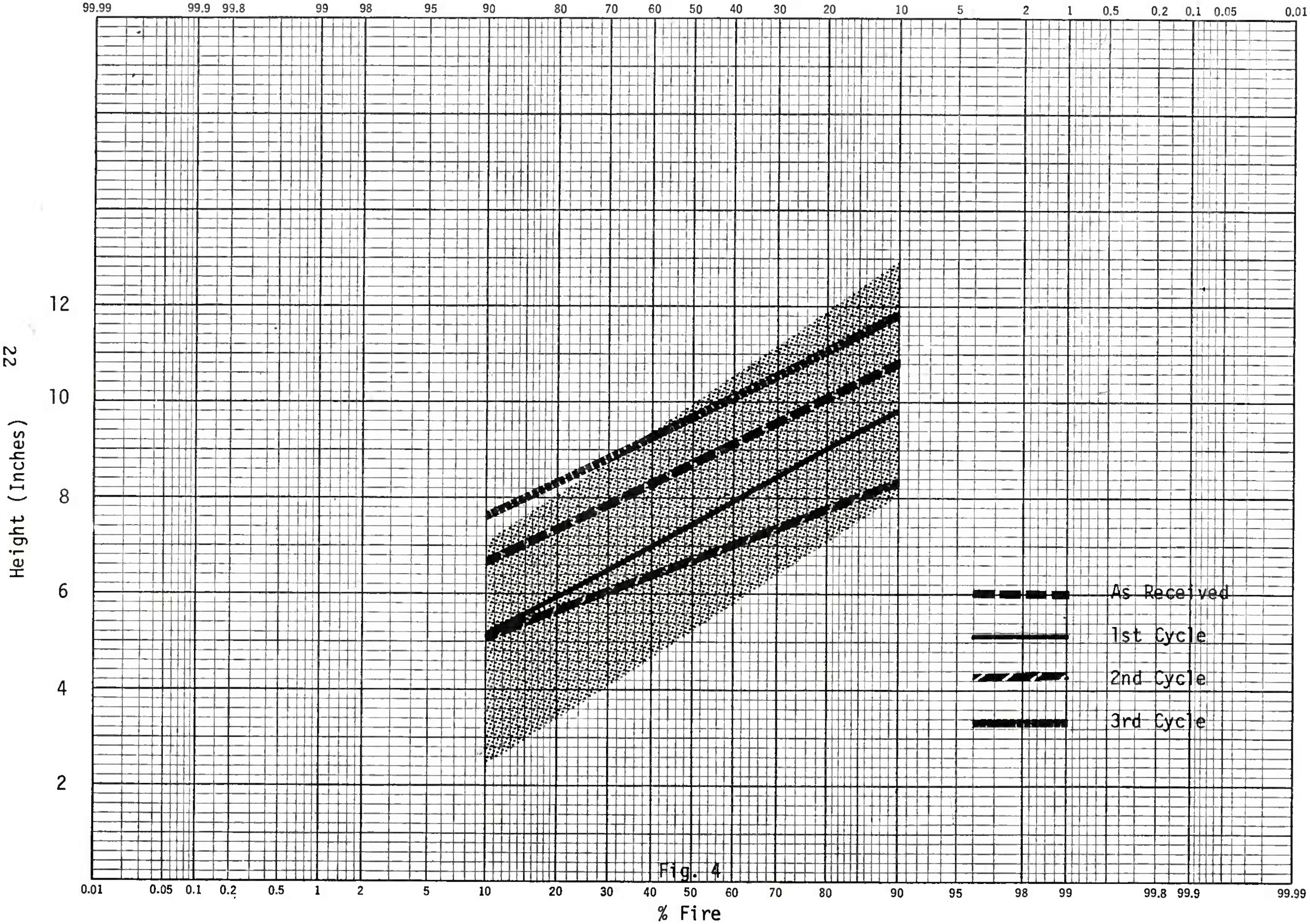


Fig. 4

Special Purpose Lead Azide
Lot #Dupont 53-17

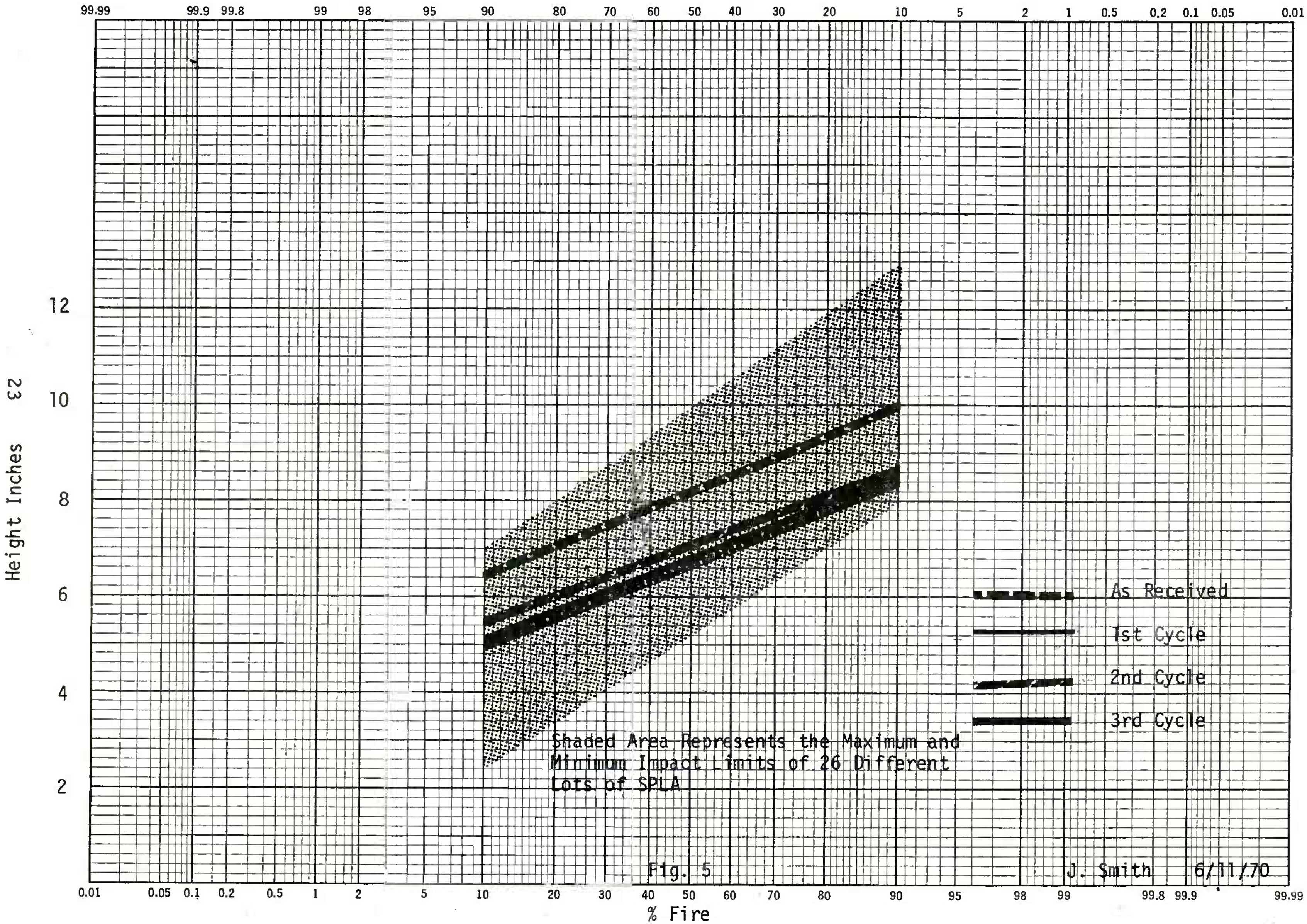


Fig. 5

Special Purpose Lead Azide
Lot #Dupont 53-44

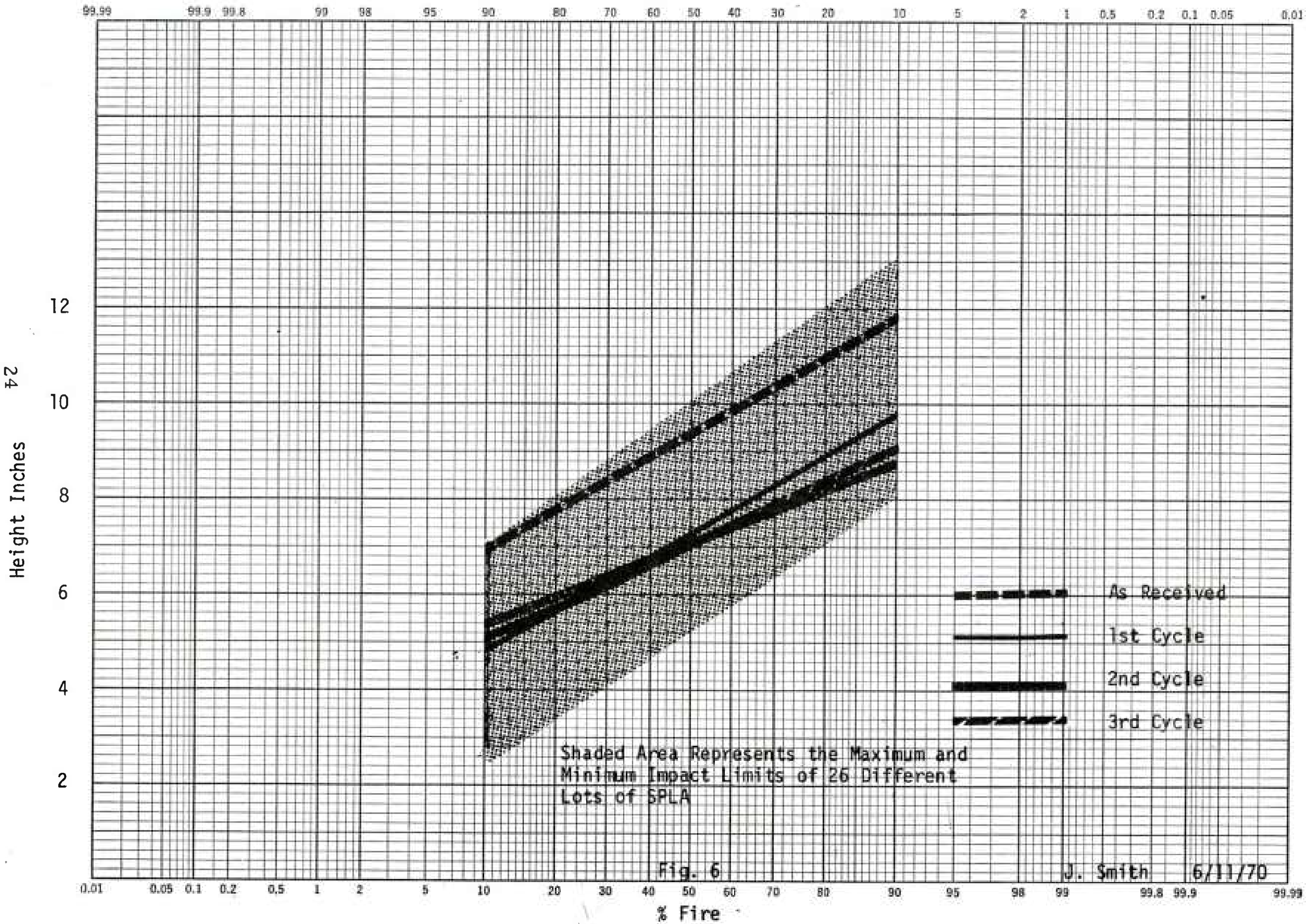


Fig. 6

Lead Azide RD 1333
Lot #OM2-2

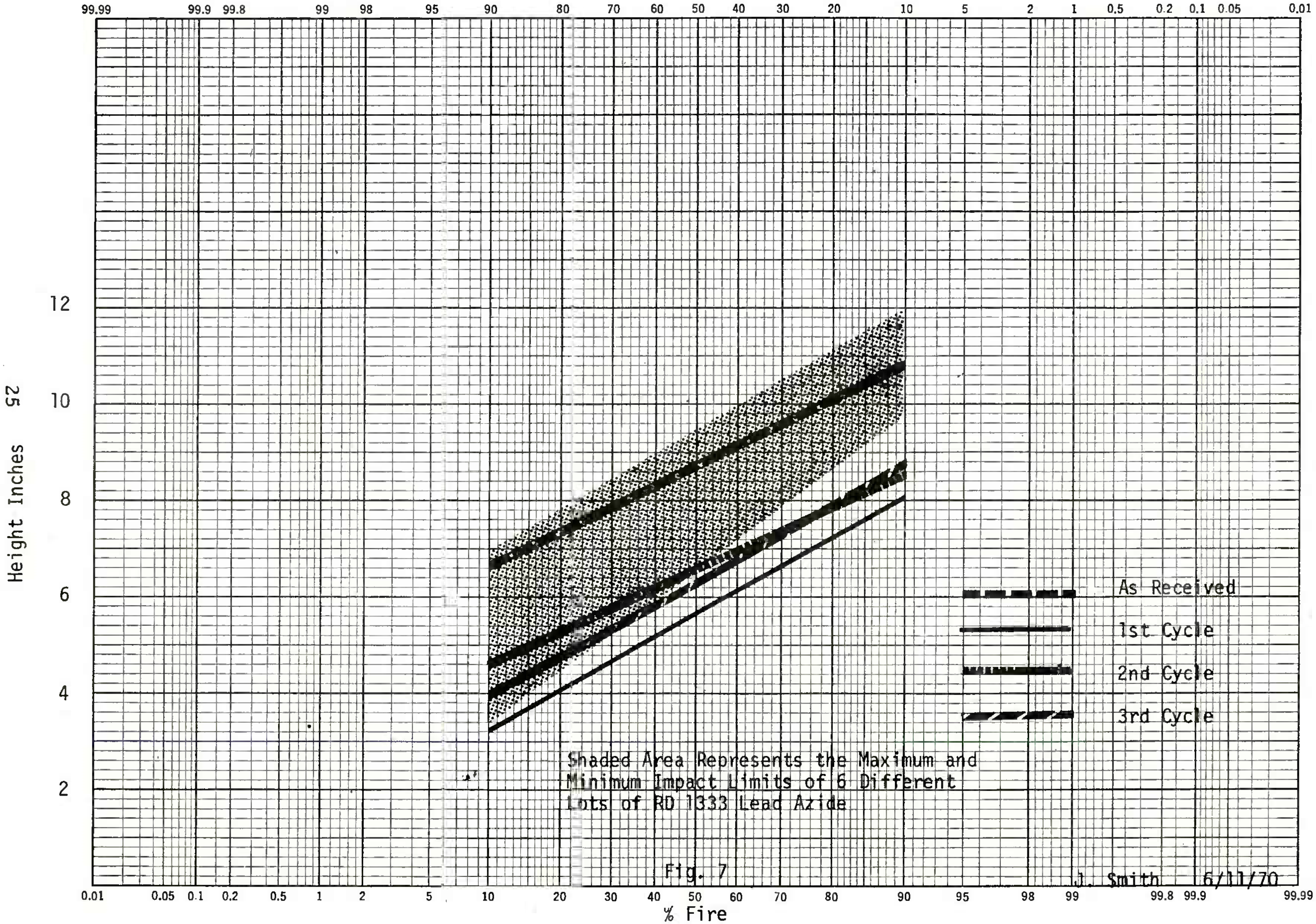


Fig. 7

Lead Azide RD 1333
Lot #Dupont 51-32-6

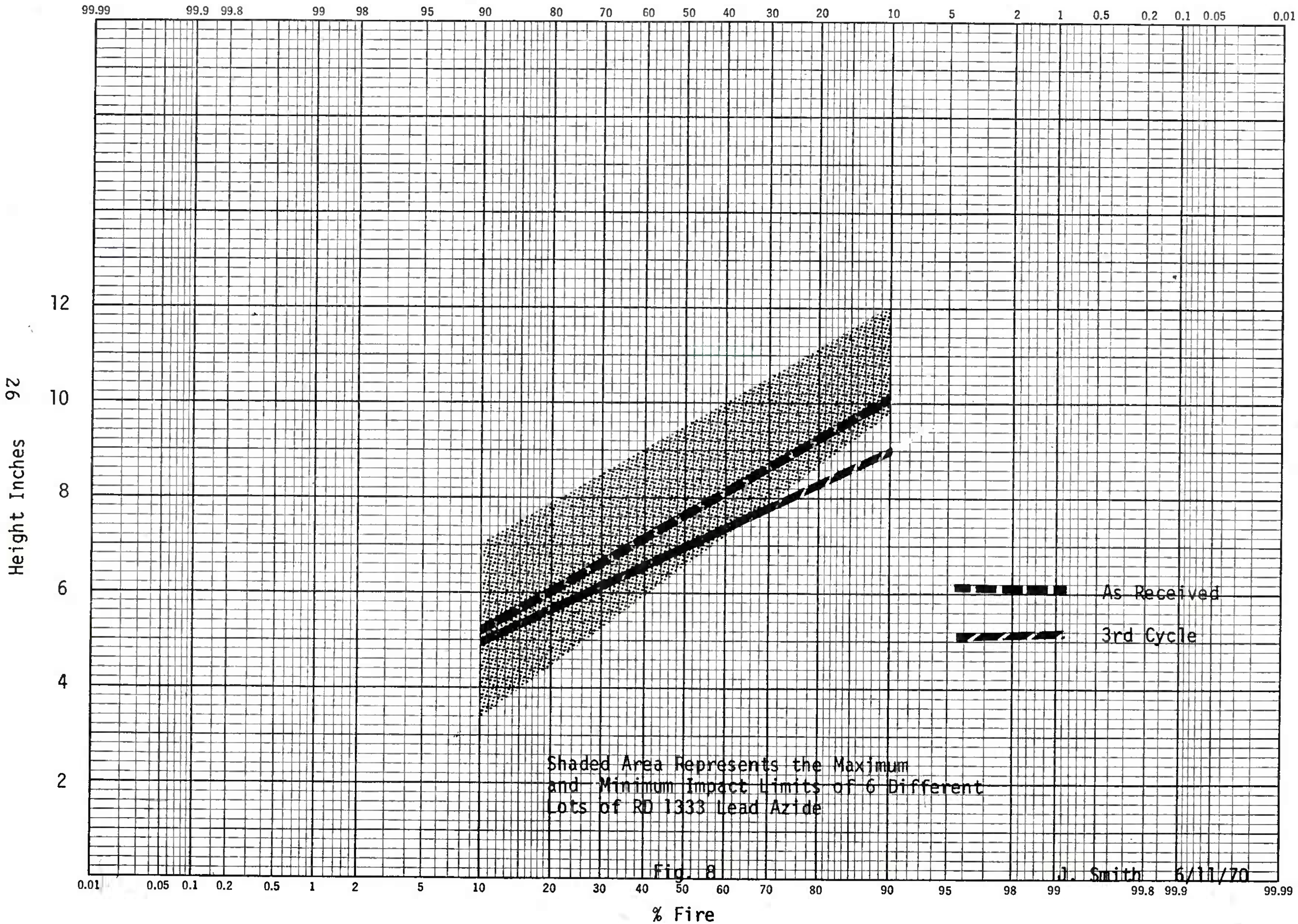


Fig. 8

SAMPLE: SPLA Lead Azide As Received Lot # DUP 53-17	**SIZE** 2.0 mg PbN_6 8.0 mg beads	**ATM.** Helium at 400 cc/min	**RUN NO.**
	REF. 10.0 mg glass beads	T: 50 °C/in; △T: 0.5 °C/in	**DATE**
	PROGRAM MODE	**SCALE SETTING**	**OPERATOR**
ORIGIN:	**RATE** 10 °C/min **, START** °C		

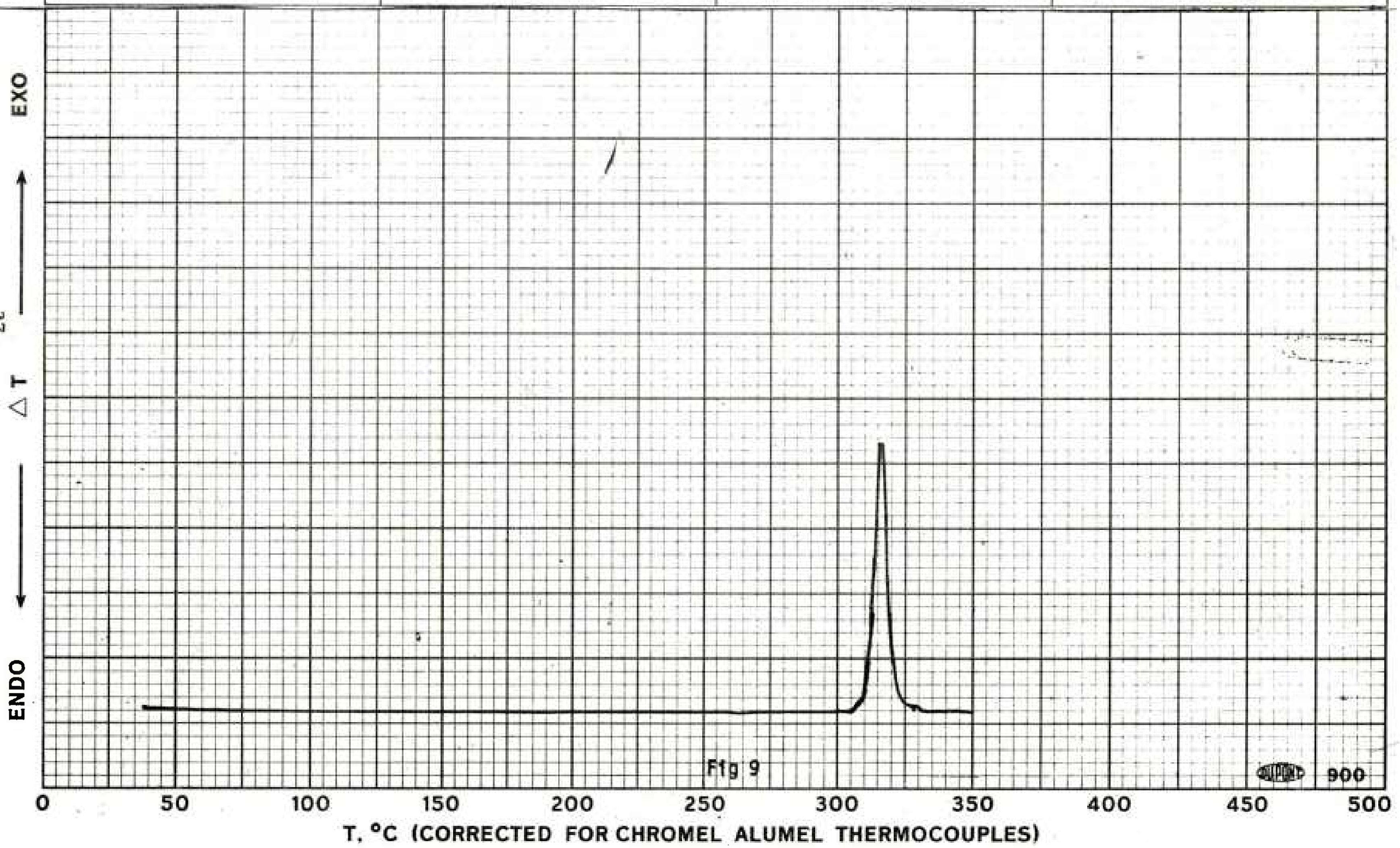


Fig 9

SAMPLE: SPLA Lead Azide 1st Cycle Lot # DUP 53-17	**SIZE** 2.0 mg PbN_6 8.0 mg beads	**ATM.** Helium 400 cc/min	**RUN NO.**
	REF. 9.5 mg glass beads	**SCALE SETTING** T: 50 °C/IN.; △T: 0.5 °C/IN.	**DATE**
	PROGRAM MODE		**OPERATOR**
ORIGIN:	**RATE** 10 °C/MIN, **START** °C		

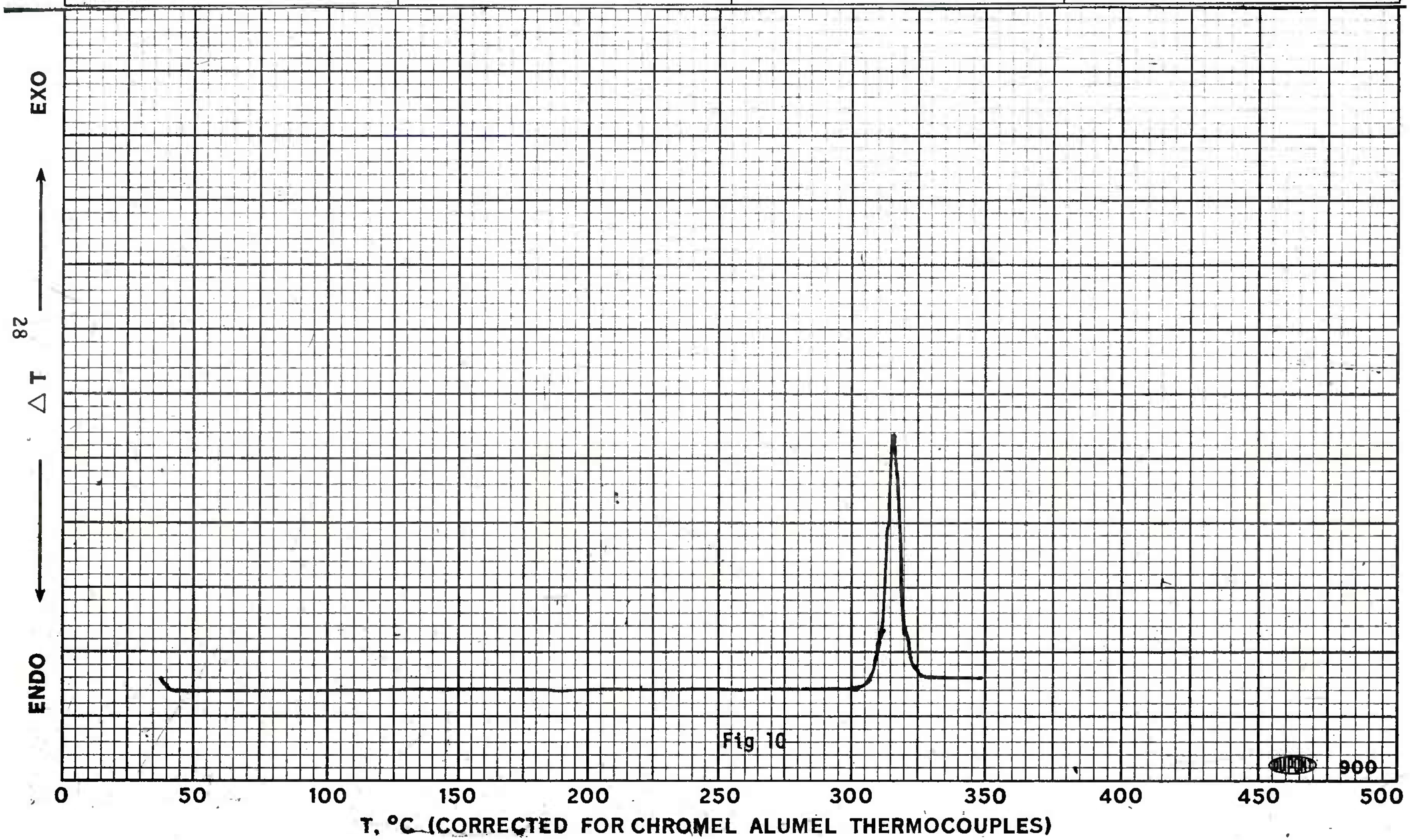
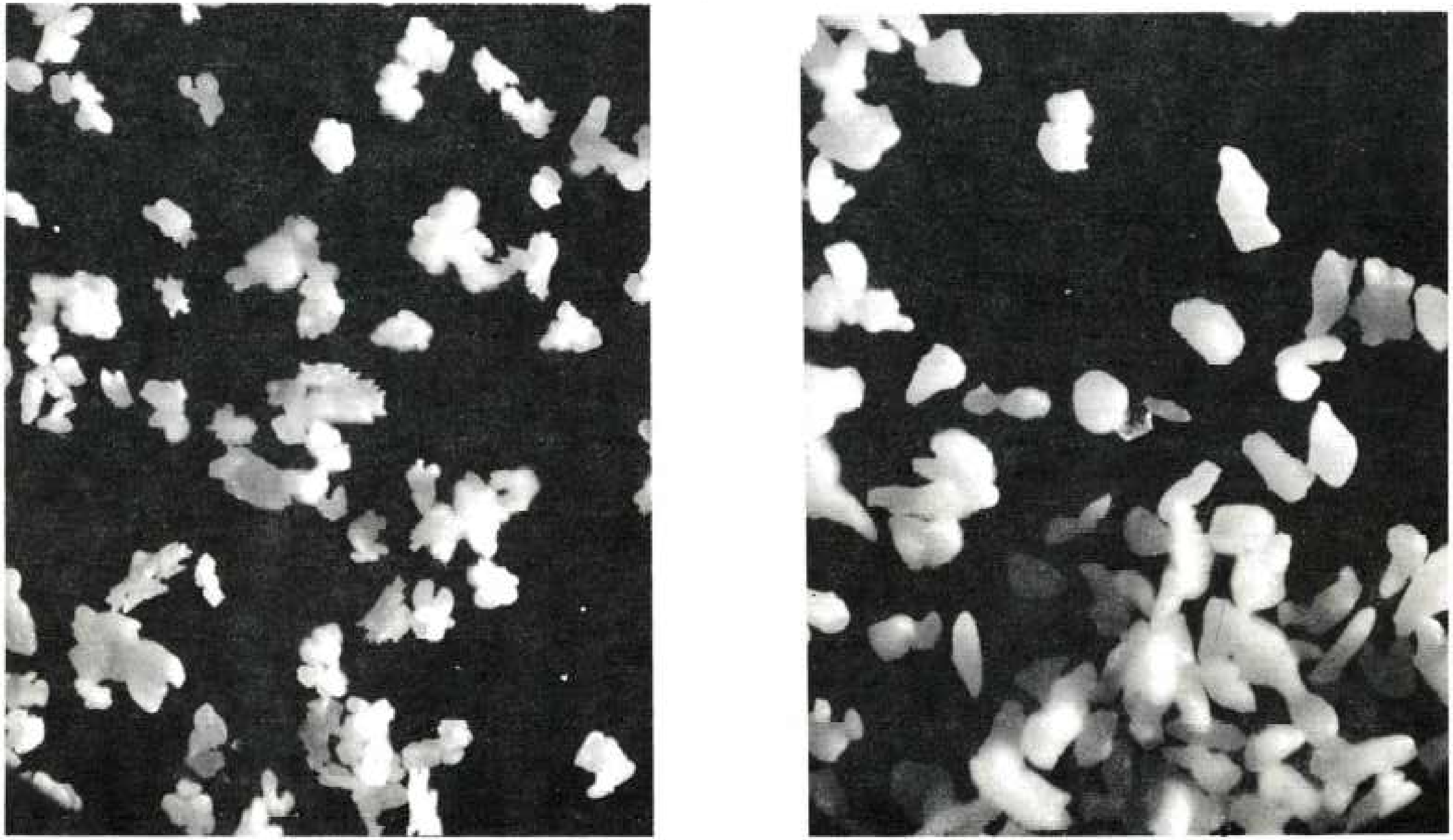


Fig 10



RD1333 Lot #OLN-2-1

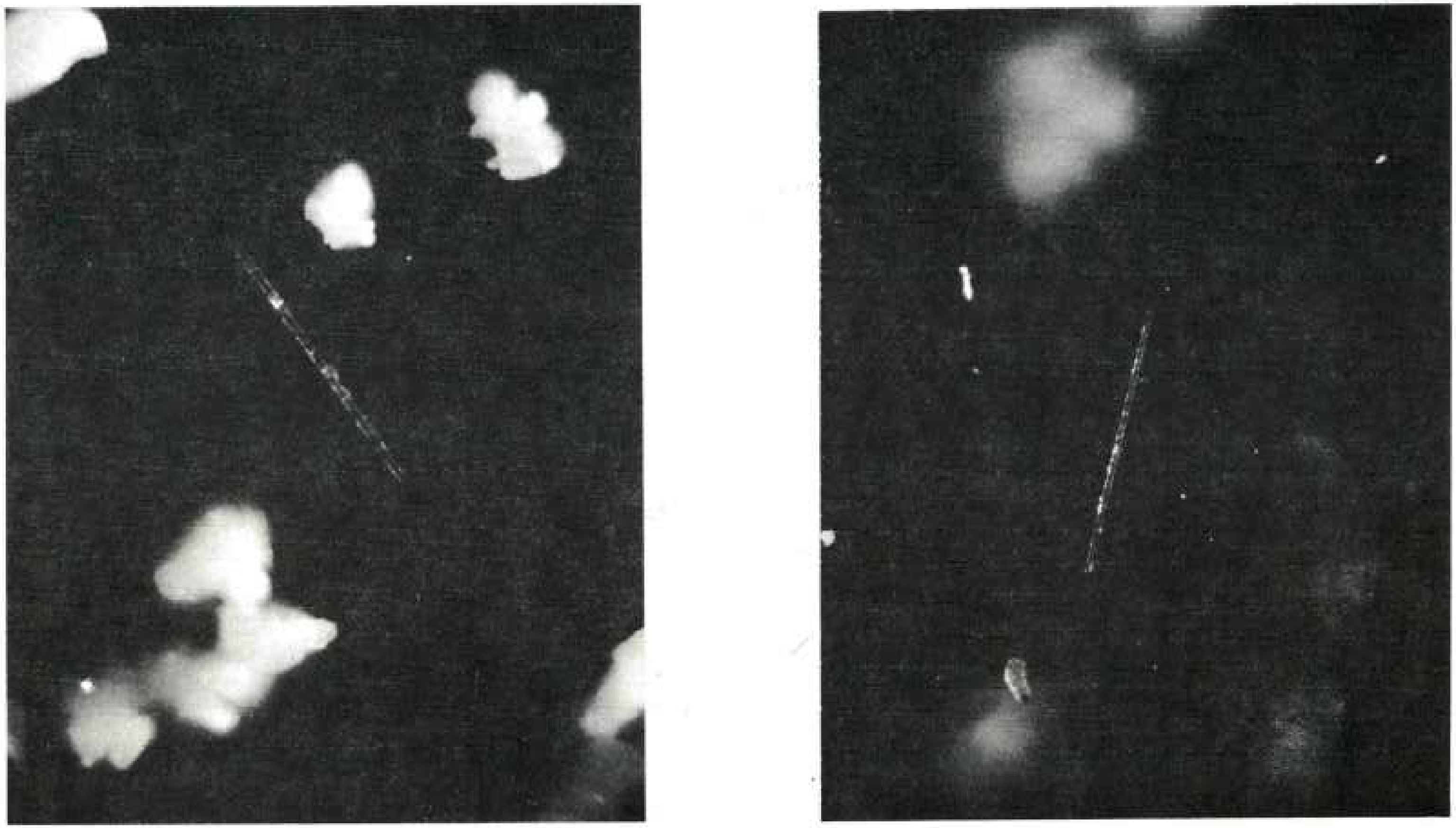
Special Purpose Lead Azide Lot #JA-4-62

Fig 11

SPLA Lot #Dup-53-17 9/25/69 1st Cycle

SPLA Lot #OM-67-5 9/25/69 1st Cycle

Fig 12



Special Purpose Lead Azide Lot #Dup-53-27 Special Purpose Lead Azide #JA-4-52 2nd Cycle

Fig 13

BALL DROP DATA FIRST SURVEILLANCE SAMPLES UNIROYAL

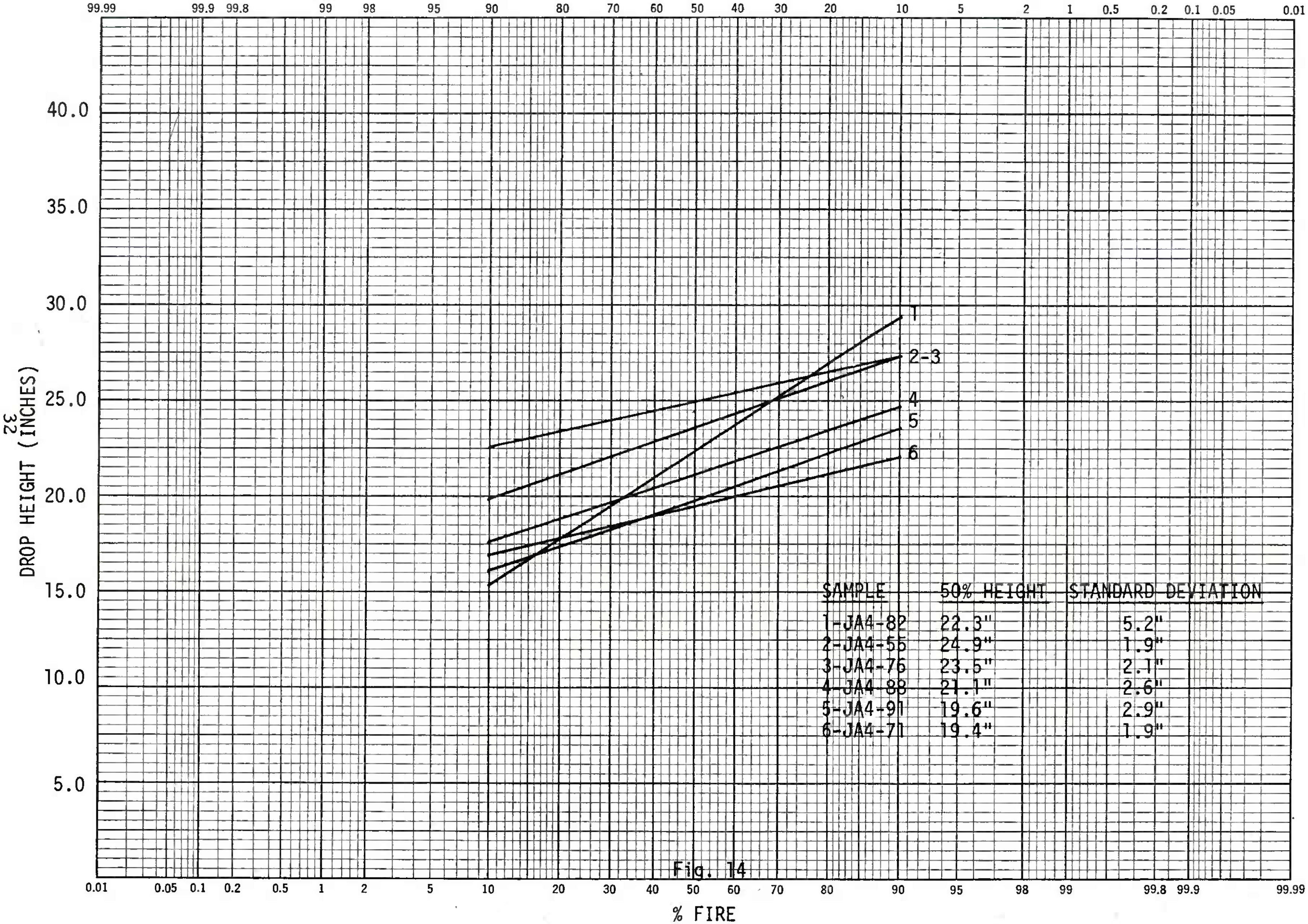
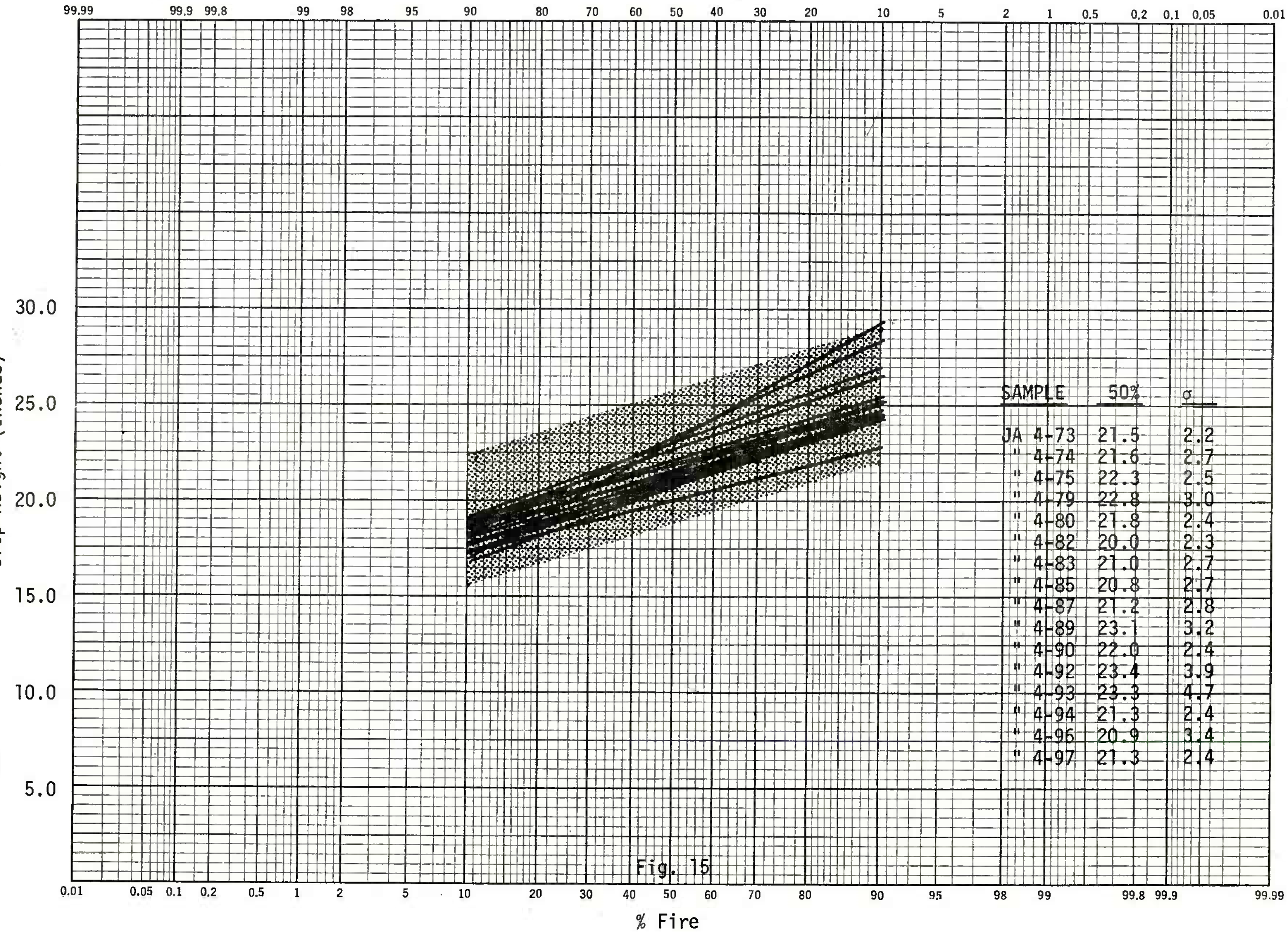


Fig. 14

Impact Sensitivity For Second Surveillance Samples Uniroyal



SAMPLE	50%	σ
JA 4-73	21.5	2.2
" 4-74	21.6	2.7
" 4-75	22.3	2.5
" 4-79	22.8	3.0
" 4-80	21.8	2.4
" 4-82	20.0	2.3
" 4-83	21.0	2.7
" 4-85	20.8	2.7
" 4-87	21.2	2.8
" 4-89	23.1	3.2
" 4-90	22.0	2.4
" 4-92	23.4	3.9
" 4-93	23.3	4.7
" 4-94	21.3	2.4
" 4-96	20.9	3.4
" 4-97	21.3	2.4

Fig. 15

BALL DROP DATA FIRST SURVEILLANCE SAMPLES   E.I. DUPONT

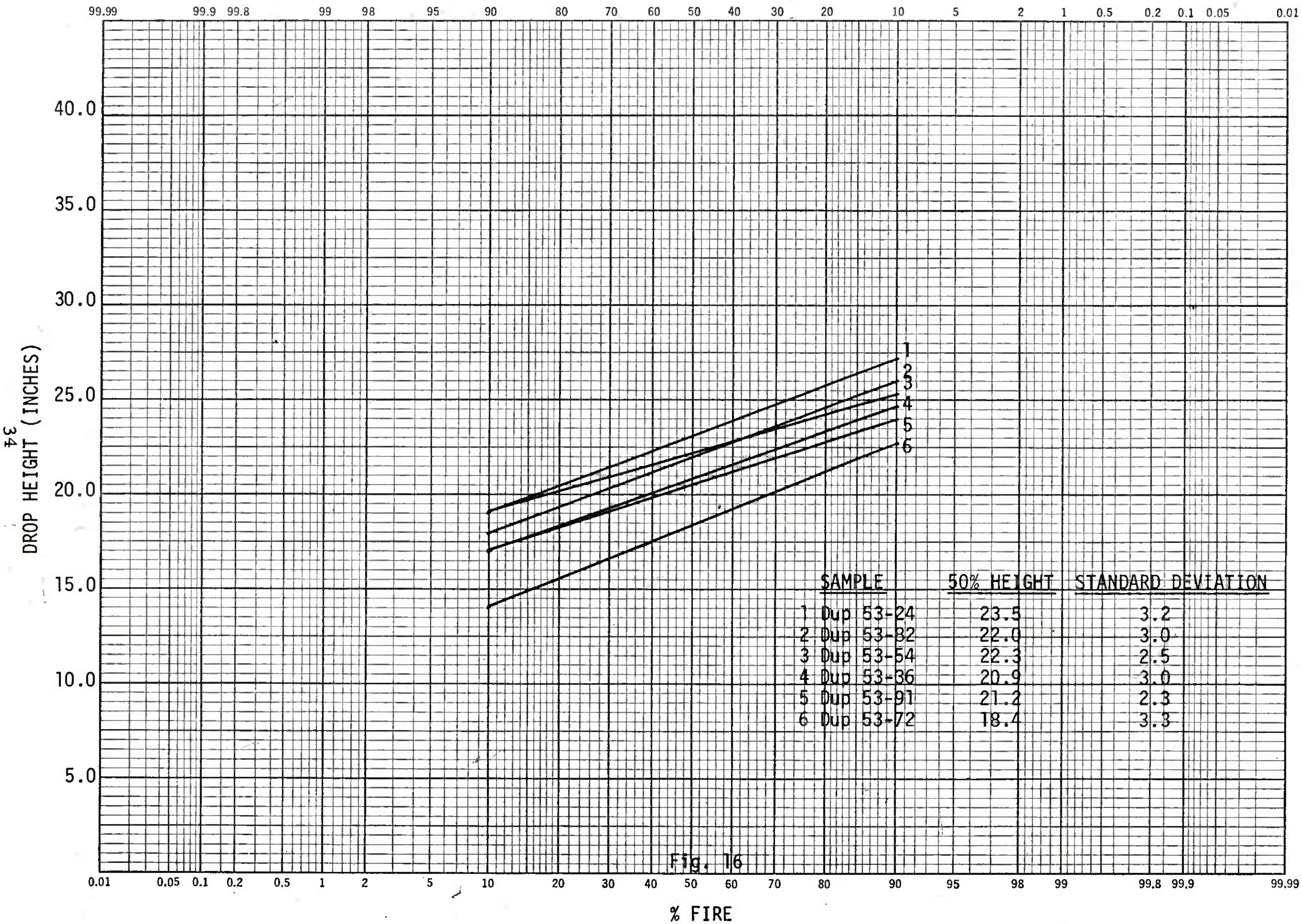


Fig. 16

Impact Sensitivity for Second Surveillance Samples   Dupont

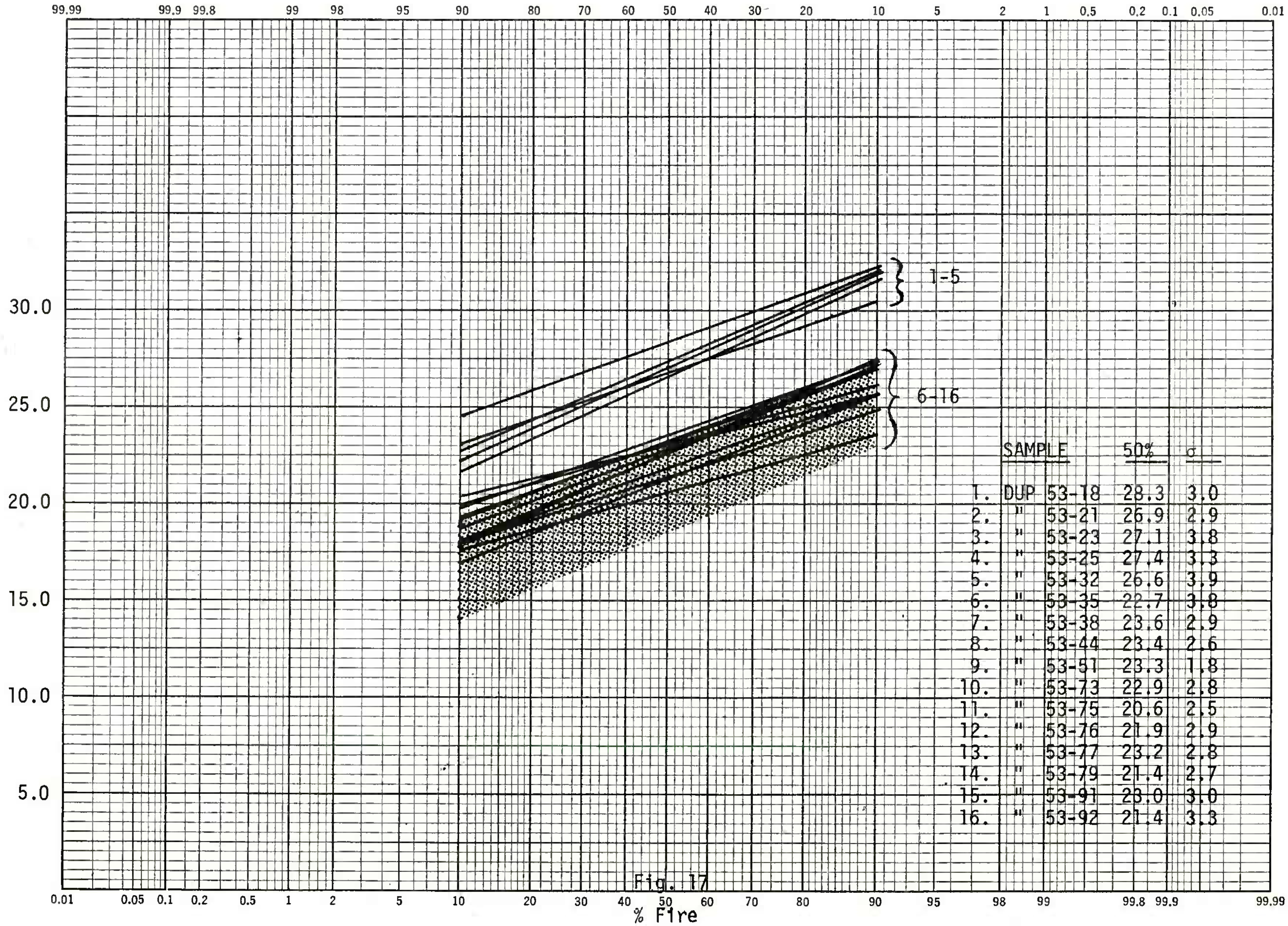


Fig. 17

	SAMPLE	50%	σ
1.	DUP 53-18	28.3	3.0
2.	" 53-21	26.9	2.9
3.	" 53-23	27.1	3.8
4.	" 53-25	27.4	3.3
5.	" 53-32	26.6	3.9
6.	" 53-35	22.7	3.8
7.	" 53-38	23.6	2.9
8.	" 53-44	23.4	2.6
9.	" 53-51	23.3	1.8
10.	" 53-73	22.9	2.8
11.	" 53-75	20.6	2.5
12.	" 53-76	21.9	2.9
13.	" 53-77	23.2	2.8
14.	" 53-79	21.4	2.7
15.	" 53-91	23.0	3.0
16.	" 53-92	21.4	3.3

Monitor Sample Tests (Surveillance)

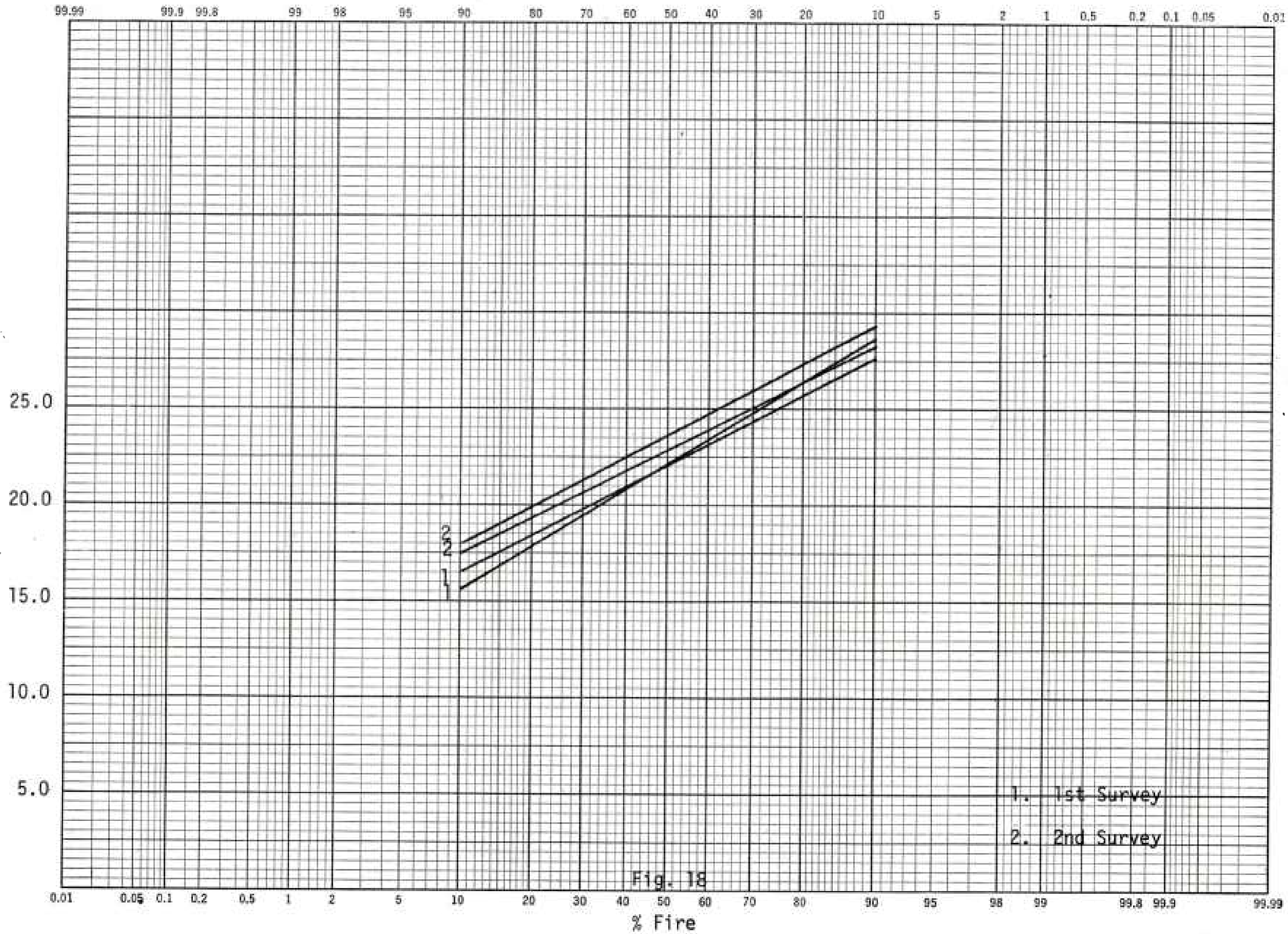
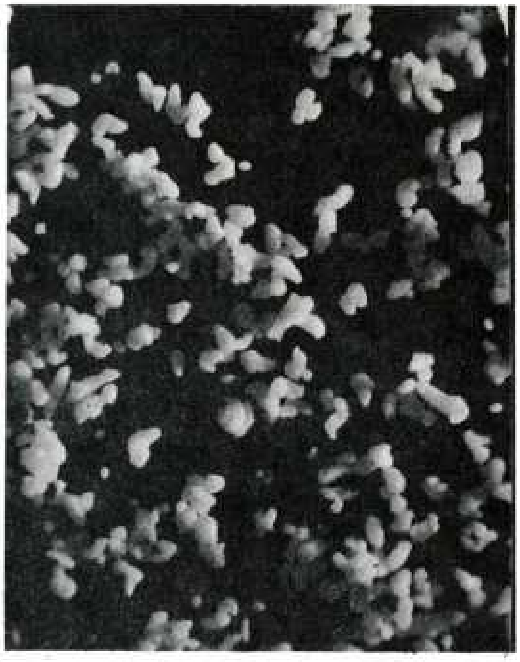
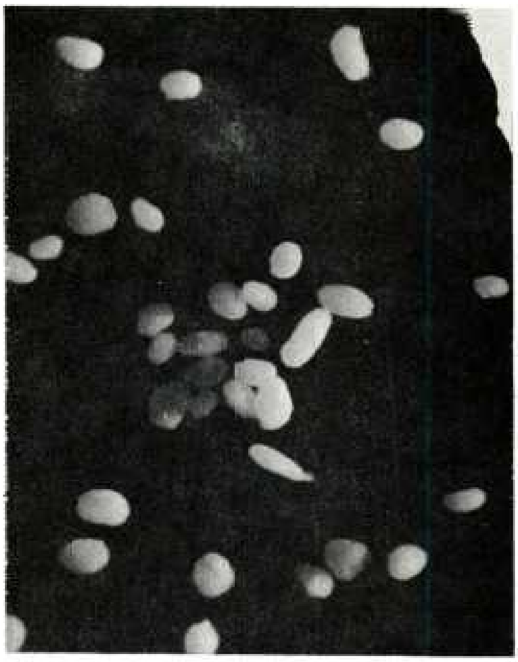


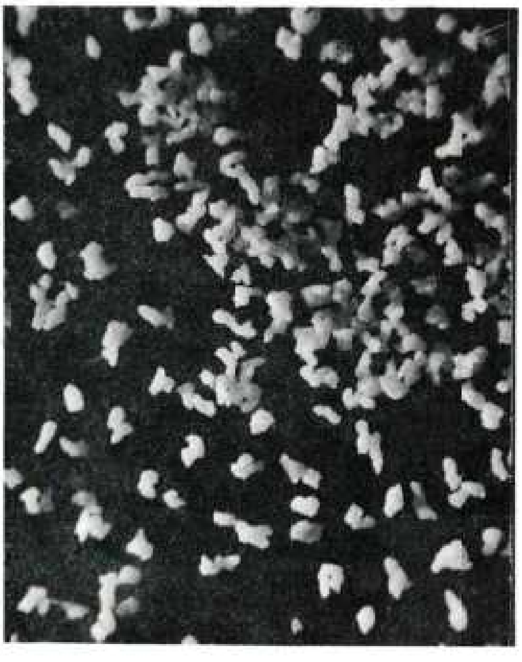
Fig. 18



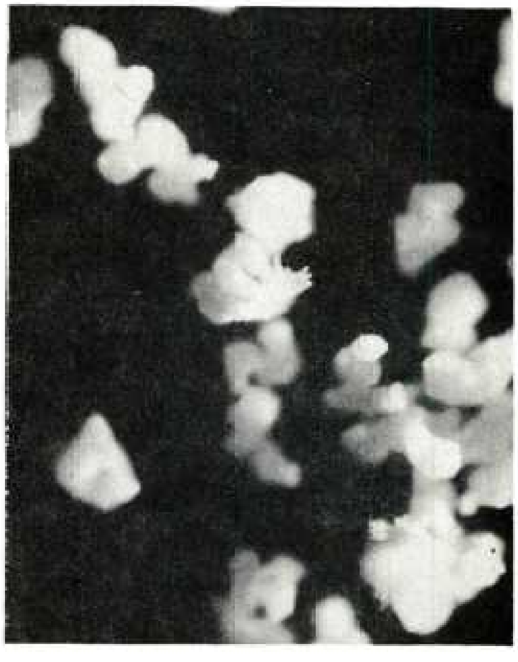
JA-4-71 X 40



JA-4-71 X 100



JA-4-76 X 40



JA-4-76 X 100

Figure 19

APPENDIX A

A LABORATORY EVALUATION OF PACKAGING MATERIALS USED IN SPECIAL PURPOSE LEAD AZIDE CONTAINERS

Explosives Division
18 August 1969
Joseph Smith

As requested by U.S. Army Material Command letter AMC-PMSA dated 7 November 1968, the Explosives Division, Picatinny Arsenal initiated a study of long term storage effects on special purpose lead azide. Discussions with APSA and Savanna Ordnance Depot personnel in regards to the sampling of lead azide for the above studies resulted in the letter AMXSV-SU dated 22 January 1969, in which it was indicated that during withdrawal of lead azide samples from storage containers deterioration of packaging materials was observed. In view of the above, it was apparent that in addition to the present studies now in progress on special purpose lead azide (SPLA) an immediate investigation was necessary to determine the nature of the deterioration and to obtain basic knowledge in regards to whether or not physical and chemical changes were occurring in lead azide storage packaging materials.

To obtain first hand information as to the present condition of metal storage containers and packaging materials, a representative of the Explosives Division visited installations where special purpose lead azide is stored. On 30 April 1969 and 4 June 1969 trips were made to Savanna Ordnance Depot and Ravenna Army Ammunition Plant. At these installations lead azide storage containers packaged by different manufacturers were opened to observe the interior condition of the container, examine packaging materials and obtain samples for study. For details of visual inspection and observations see Appendices B and C.

Visual inspection during unpackaging of selected drums showed that the lead azide was packaged in a variety of ways. DuPont and Unircyal manufactured materials were packaged in a similar manner (see Figure 1 and 3) however, the Olin Mathieson manufactured material was packaged quite differently (Figure 5).

Inspection of the contents of the drums verified previous statements as to their condition. Therefore, it was deemed necessary to rigidly evaluate them. Storage liquids (Figures 2, 4, and 6) as well as sawdust materials (Figure 7) were carefully sampled and shipped to the Explosives Division. The following is a report of the laboratory evaluation of these materials.

<u>Selection of Drums and Sampling of Packaging Materials</u>:

The important criteria for sample selection are manufacturer and date of manufacture. Considering that the lead azide storage samples represent different <u>manufacturers</u> with different lot numbers and <u>manufacture dates</u>, every effort was made to select representative samples from each installation visited.

Samples were taken from various positions in the storage drum as follows:

The solution in contact with the drum was sampled from the top of the storage drum prior to opening the drum liner. After siphoning off several inches of liquid the drum liner was visible, siphoning was continued until approximately half of the drum liner was exposed. The drum liner was opened and sufficient sawdust was removed so that the bag containing the lead azide was easily accessible. Before each bag was opened the outside of the bag was thoroughly washed down with a fresh 50/50 water-alcohol solution. Also, before opening the bag, particular attention was given to removal of sawdust from deep folds and creases to prevent contamination of one bag into another. Liquids inside the bag containing lead azide were sampled from the top of the bag. For additional details see Appendices B and C.

Experimental

Determination of Hydrazoic Acid:

Using a technique recently developed by the Explosives Division, the concentration of azide ion was determined in the liquid samples. Table 1 shows milligrams of azide ion per liter and the molar concentration of hydrazoic acid found in alcohol-water solutions from storage containers of lead azide packaged by different manufacturers.

Determination of Iron:

The solutions were centrifuged and the insoluble residue was carefully separated. The concentration of iron in both phases was determined by a combination of classical and colorimetric techniques. Table 2 shows the concentration of iron in the liquid phase expressed as milligrams of iron per liter and as molar concentration. Table 3 shows concentration of insoluble residues (recovered by centrifuging) expressed as milligrams per liter. The percentage of iron found in this residue is also given.

Determination of Soluble Organic Material Extracted by Alcohol-Water Storage Solutions:

During long term storage significant amounts of organic materials are extracted from the sawdust by the water-alcohol storage solution. Table 4 shows the concentration of soluble organic materials expressed in grams per liter.

Determination of Alcohol Content and pH of Storage Solutions:

The percent alcohol present was determined using density techniques. The densities of the solutions were determined by means of a

Leach pycnometer. From tables of density versus percent alcohol the solution compositions were determined. In addition, the pH of the solutions were measured using a Beckman Expandomatic Meter. Table 5 shows the pH and percent alcohol (by wt.), along with the visual evaluation of the drum interiors.

Discussion of Results

Hydrazoic acid is generated as a decomposition product of lead azide hydrolysis. A comparison of the results presented in Table 1 shows that in materials packaged by DuPont (1967 vs 1968) and Olin Mathieson (1966 vs 1968) the hydrazoic acid molar concentration in the liquid in contact with the drum increased with length of storage time. Also, the hydrazoic acid molar concentration is much greater in the inner bags containing the lead azide when it is packaged in multiple polyethylene bags than when it is packaged in a rubberized canvas bag. This indicates that the diffusion of hydrazoic acid is much slower through multiple polyethylene bags than it is through the rubberized canvas bags used by Olin Mathieson.

The data in Table 2 shows that the concentration of iron in the storage liquids that are in immediate contact with the metal drum increases with length of storage time. Also, it can be seen that in general when the lead azide is packaged in a rubberized canvas bag the iron content of the solution in contact with the drum is approximately the same as that of the solution in contact with the lead azide. As in the case of hydrazoic acid it is again shown that passage of ions is not restricted by the rubberized canvas bag. In cases where the lead azide is enclosed by two or three polyethylene bags, analyses of the solution in individual bags revealed that the iron concentration decreases going from the drum inward to the bag containing the lead azide. Here again is proof that the diffusion of ions is much slower through multiple layers of polyethylene than through rubberized canvas.

Iron and hydrazoic acid have been shown to be present in the storage liquids, so it is reasonable to assume that the ferric azide complex $[FeN_3]^{++}$ is present. However, the pH values obtained for these solutions were at borderline conditions for this reaction to occur[1]. In order to verify the existence of the complex, spectrophotometric evaluations were made in the strong absorption region (460 mμ) of this complex. Absorptions at this wavelength was obtained for all colored solutions. The data presented in Tables 1 and 2 show that when rubberized canvas bags are used the mole to mole ratio of iron to HN_3 in the storage solution is not 1:1, with HN_3 being in excess. Therefore additional HN_3 is always available for continued reaction with the drum.

In most cases, the storage solutions showed turbidity. These

solutions were centrifuged and the insoluble residue was carefully separated before solution analyses were performed. Residue weights are given in Table 3 and show that the amount of insoluble residue present increases with length of storage time. The increase in residue amounts are considered to be quite large for the elapsed storage time. Also, it is believed that residue amounts will be found to be even greater at the bottom of the drum. The Olin Mathieson packaged material (packaged 9/66) contained the largest quantity of residue. The residue (OM-66-28) recovered from the liquid in contact with the drum contained 34.47% iron. Also gas evolution was observed when it was reacted with Ceric Ammonium Nitrate solution indicating the presence of azide ion; chemical analyses were carried out and the results showed azide to be present to the amount of .01%. Loss on ignition (amount of organic material present) was 47.4% by weight. In comparison, the residue recovered from the solution in contact with the lead azide contained 7.93% on ignition. No detonations occurred from "match tests" or ignitions.

Ambient temperature fluxuations which cause solvation and subsequent recrystallization of the SPLA could result, under storage conditions, in a doped form of crystal. As proven by this investigation, the dopant ions could easily be $[FeN_3]^{++}$, or Fe^{+++} compensated with a bivalent metal ion. The composition of the steel used for fabrication of the storage drums would lead one to suspect the presence of manganese and the formation of the bivalent Mn^{++} ion resulting from reaction with the HN_3 present in the solutions. To investigate the validity of this hypothesis it was decided to use EPR techniques.

It was felt that the residue most closely fitting the stated requirements would be one obtained from the solution between the diaper cloth and duck cloth bags in the Olin Mathieson package configuration (Figure 5). Since the diaper cloth was the filter medium for the production filtration it should retain the original azide crystals. Also, the duck cloth bag is of a close enough weave to keep out large particles from the surrounding medium. Therefore residues from this area should contain a product resulting from the reaction of ions that have passed out from the lead azide bag and in from the drum area. The EPR spectra obtained from this residue gave large Fe^{+++} and Mn^{++} peaks resulting from the presence of these metallic ions in a crystal lattice.

The solubility of various organic components of the sawdust in the alcohol/water solution is apparent from the results given in Table 4. These organics can be waxes, tannins, or oils; and their concentrations will vary with the type of sawdust used. Another contributor

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1. Wallace and Dukes, J. Chem. Phys., 65, 2094 (1961).

to the amount of organics present in storage solutions could be dissolved shellac and varnish sometimes used as an inner coating for drums. It is understood that in some cases drums had been coated with shellac or varnish but no such coatings were observed in the drums that were opened. However, two drums had a black deposit on the inner wall which easily rubbed off. This may have been an insoluble portion of a shellac or varnish coating.

The organic extraction process is a function of the alcohol content of the solution and, as shown in Table 5, these are quite high in many cases. In fact it is felt that they are large enough to assume that the alcohol content of the solution must at times be greater than 50%.

Recommendations:

On the basis of the findings reported here the following are recommended:

1. The packaging of lead azide in rubberized canvas bags should be stopped.

2. An investigation should be started to find a more suitable material than sawdust for cushioning.

3. Visual observation of the plastic tape used to secure the packaging bags revealed that it had already lost its adhesive properties. Tying the bags with a strong cotton cord would be more suitable.

4. It is felt that the Olin Mathieson packaged SPLA should be repackaged using the multiple polyethylene bag configuration used by other manufacturers. However, prior to any repackaging operations the inspection suggested under Discussion of Results pertaining to the opening of a few drums and evaluating their condition from top to bottom should be performed.

5. This investigation points out that knowledge of rates of permeation, as well as rates and mechanisms of reactions must be obtained if reasonable predictions of safe storage times are to be made.

6. As shown in Figures 1, 3, and 5, a "drum liner" bag is used to contain all of the packaging materials. The purpose of this "envelope" is to keep the sawdust in such a position so as to surround the inner bags. In the cases where a canvas bag was used (DuPont and Uniroyal) this configuration was maintained. However, in the case of Olin Mathieson packaging where a jute bag (or liner) is employed some drums showed deterioration of the liner. This allows all of the sawdust to settle to the bottom and only the bottom of the drum is cushioned. It is recommended that the use of Jute materials as a liner be discontinued.

7. It is recommended that the feasibility of using polyethylene (or other suitable plastics) lined drums be investigated.

TABLE 1

HYDRAZOIC ACID CONCENTRATION IN STORAGE LIQUIDS

Sample Lot No.	Date Mfg.	Liquid Sampled	Milligrams N_3^-/Liter	Hydrazoic Acid Molar Concentration
		Olin Mathieson Packaged Special Purpose Lead Azide		
OM-66-28	9/66	Soln in Cont. w/metal drum	9.20	0.21×10^{-3}
		Soln inside rubberized bag	50.0	0.68×10^{-3}*
OM-1-15	1/68	Soln in cont. w/metal drum	2.00	0.05×10^{-3}
		Soln inside rubberized bag	68.0	1.07×10^{-3}
OM-1-17	2/68	Soln in cont. w/metal drum	-	-
		Soln inside rubberized bag	47.2	0.59×10^{-3}
OM-1-19	2/68	Soln in cont. w/metal drum	2.00	0.05×10^{-3}
		Soln inside rubberized bag	54.0	0.75×10^{-3}
OM-1-22	4/68	Soln in cont. w/metal drum	1.20	0.03×10^{-3}
		Soln inside rubberized bag	28.0	0.14×10^{-3}
OM-1-24	5/68	Soln in Cont. w/metal drum	2.80	0.07×10^{-3}
		Soln inside rubberized bag	30.0	0.19×10^{-3}
		Uniroyal Packaged Special Purpose Lead Azide		
JA-4-50	6/67	Soln in cont. w/metal drum	6.00	0.14×10^{-3}
		Soln in outermost polyethylene bag	6.00	0.14×10^{-3}
		Soln in middle polyethylene bag	6.00	0.21×10^{-3}
		Soln in polyethylene bag containing lead azide	144.0	2.8×10^{-3}
		DuPont Packaged Special Purpose Lead Azide		
Dup-53-35	7/67	Soln in cont. w/metal drum	10.0	0.23×10^{-3}
		Soln in outer polyethylene bag	67.6	1.57×10^{-3}
		Soln inside polyethylene bag containing lead azide	175.0	3.57×10^{-3}
Dup-53-82	2/68	Soln in cont. w/metal drum	2.00	0.05×10^{-3}
		Soln in outer polyethylene bag	28.4	0.66×10^{-3}
		Soln in polyethylene bag containing lead azide	144.0	2.8×10^{-3}

*Solutions sampled from bags containing lead azide corrected for solubility of lead azice in 50/50 water-alcohol solution.

TABLE 2

IRON CONCENTRATION IN STORAGE LIQUIDS

Sample Lot. No.	Date Mfg.	Liquid Sampled	Milligrams Fe/Liter	Iron Molar Concentration
		Olin Mathieson Packaged Special Purpose Lead Azide		
OM-66-28	9/66	Soln in cont. w/metal drum	2.56	0.05×10^{-3}
		Soln inside rubberized bag	2.40	0.043×10^{-3}
OM-1-15	1/68	Soln in cont. w/metal drum	1.52	0.027×10^{-3}
		Soln inside rubberized bag	1.20	0.022×10^{-3}
OM-1-17	2/68	Soln in cont. w/metal drum	0.48	0.009×10^{-3}
		Soln inside rubberized bag	1.12	0.020×10^{-3}
OM-1-19	2/68	Soln in cont. w/metal drum	0.76	0.014×10^{-3}
		Soln inside rubberized bag	0.88	0.016×10^{-3}
OM-1-22	4/68	Soln in cont. w/metal drum	0.76	0.014×10^{-3}
		Soln inside rubberized bag	0.88	0.016×10^{-3}
OM-1-24	5/68	Soln in cont. w/metal drum	0.40	0.007×10^{-3}
		Soln inside rubberized bag	0.36	0.006×10^{-3}
		Uniroyal Packaged Special Purpose Lead Azide		
JA-4-50	6/67	Soln in cont. w/metal drum	17.0	0.304×10^{-3}
		Soln in outermost polyethylene bag	3.4	0.06×10^{-3}
		Soln in middle polyethylene bag	1.92	0.034×10^{-3}
		Soln inside polyethylene bag containing lead azide	0.48	0.0009×10^{-3}
		DuPont Packaged Special Purpose Lead Azide		
Dup-53-35	7/67	Soln in cont. w/metal drum	27.2	0.49×10^{-3}
		Soln in outer polyethylene bag	2.72	0.049×10^{-3}
		Soln inside polyethylene bag containing lead azide	1.12	0.02×10^{-3}
Dup-53-82	2/68	Soln in cont. w/metal drum	13.6	0.22×10^{-3}
		Soln in outer polyethylene bag	.40	0.007×10^{-3}
		Soln inside polyethylene bag containing lead azide	.48	0.009×10^{-3}

TABLE 3

CONCENTRATION OF IRON IN INSOLUBLE RESIDUE RECOVERED FROM STORAGE LIQUIDS

Sample Lot No.	Date Mfg.	Liquid Sampled	Milligrams insol. Residue/Liter	% Iron In Residue
		Olin Mathieson Packaged Special Purpose Lead Azide		
OM-66-28	9/66	Soln in cont. w/metal drum	689.6	34.47
		Soln inside rubberized bag	342.7	7.93
OM-1-15	1/68	Soln in cont. w/metal drum	71.6	6.51
		Soln inside rubberized bag	38.4	0.81
OM-1-17	2/68	Soln in cont. w/metal drum	50.0	1.51
		Soln inside rubberized bag	26.4	0.37
OM-1-19	2/68	Soln in cont. w/metal drum	65.8	0.75
		Soln inside rubberized bag	25.5	1.48
OM-1-22	2/68	Soln in cont. w/metal drum	36.2	4.88
		Soln inside rubberized bag	49.8	0.47
OM-1-24	5/68	Soln in cont. w/metal drum	40.2	0.18
		Soln inside rubberized bag	120.4	0.32
		Uniroyal Packaged Special Purpose Lead Azide		
JA-4-50	6/67	Soln in cont. w/metal drum	not analyzed	
		Soln in outermost polyethylene bag	not analyzed	
		Soln in middle polyethylene bag	40.8	1.50
		Soln in polyethylene bag containing lead azide	44.8	1.33
		DuPont Packaged Special Purpose Lead Azide		
Dup-53-35	7/67	Soln in cont. w/metal drum	201.6	9.94
		Soln in outer polyethylene bag	24.4	1.55
		Soln in polyethylene bag containing lead azide	14.8	4.00
Dup-53-82	2/68	Soln in cont. w/metal drum	13.8	3.60
		Soln in outer polyethylene bag	7.5	0.98
		Soln in polyethylene bag containing lead azide	13.8	0.48

TABLE 4

CONCENTRATION OF SOLUBLE ORGANIC MATERIALS IN ALCOHOL-WATER STORAGE SOLUTIONS

Olin Mathieson Packaged Special Purpose Lead Azide

Sample Lot. No.	Date Mfg.	Liquid Sampled	Extractables Grams/Liter
OM-66-28	9/66	Soln in cont. w/metal drum	3.32
		Soln inside rubberized bag	2.08
OM-1-15	1/68	Soln in cont. w/metal drum	7.40
		Soln inside rubberized bag	2.80
OM-1-17	2/68	Soln in cont. w/metal drum	5.00
		Soln inside rubberized bag	1.60
OM-1-19	2/68	Soln in cont. w/metal drum	3.60
		Soln inside rubberized bag	2.00
OM-1-22	4/68	Soln in cont. w/metal drum	2.00
		Soln inside rubberized bag	1.84
OM-1-24	5/68	Soln in cont. w/metal drum	3.26
		Soln inside rubberized bag	1.40
Uniroyal Packaged Special Purpose Lead Azide			
JA-4-50	6/67	Soln in cont. w/metal drum	4.80
		Soln in outermost polyethylene bag	4.00
		Soln in middle polyethylene bag	3.20
		Soln inside polyethylene bag containing lead azide	0.80
DuPont Packaged Special Purpose Lead Azide			
Dup-53-35	7/67	Soln in cont. w/metal drum	5.44
		Soln in outer polyethylene bag	2.76
		Soln inside polyethylene bag containing lead azide	1.08
Dup-53-82	2/68	Soln in cont. w/metal drum	4.80
		Soln in outer polyethylene bag	3.60
		Soln inside polyethylene bag containing lead azide	

TABLE 5

ALCOHOL CONTENT AND pH OF STORAGE SOLUTIONS

Olin Mathieson Packaged Special Purpose Lead Azide

Sample Lot. No.	Date Mfg.	Liquids Sampled	pH	Sp.G.	% Alcohol by Wgt.	Visual Inspec. of Drum inter.
OM-66-28	9/66	Soln in cont. w/metal drum	5.70	.922	46	Major Rust
		Soln inside rubberized bag	5.50	.951	32	
OM-1-15	1/68	Soln in cont. w/metal drum	5.50	.851	77	Moderate Rust
		Soln inside rubberized bag	5.90	.862	72	
OM-1-17	2/68	Soln in cont. w/metal drum	6.35	.845	79	Minor/Moder. Rust
		Soln inside rubberized bag	6.30	.887	62	
OM-1-19	2/68	Soln in cont. w/metal drum	6.95	.838	82	Minor/Inciden-tal Rust
		Soln inside rubberized bag	6.70	.851	77	
OM-1-22	4/68	Soln in cont. w/metal drum	6.55	.836	83	Minor/Inciden-tal Rust
		Soln inside rubberized bag	6.60	.859	74	
OM-1-24	5/68	Soln in cont. w/metal drum	6.15	.817	90	Minor/Inciden-tal Rust
		Soln inside rubberized bag	6.75	.825	87	

Uniroyal Packaged Special Purpose Lead Azide

Sample Lot. No.	Date Mfg.	Liquids Sampled	pH	Sp.G.	% Alcohol by Wgt.	Visual Inspec. of Drum inter.
JA-4-50	6/67	Soln in cont. w/metal drum	5.90	.908	53	Moderate Rust
		Soln in outermost polyethylene	5.50	.924	45	
		Soln in middle polyethylene	5.85	.913	50	
		Soln inside polyethylene bag containing lead azide	6.50	.941	37	

DuPont Packaged Special Purpose Lead Azide

Sample Lot. No.	Date Mfg.	Liquids Sampled	pH	Sp.G.	% Alcohol by Wgt.	Visual Inspec. of Drum inter.
Dup-53-35	7/67	Soln in cont. w/metal drum	5.80	.886	62	Moderate Rust
		Soln in outer polyethylene	6.35	.891	60	
		Soln inside polyethylene bag containing lead azide	6.50	.919	48	
Dup-53-82	2/68	Soln in cont. w/metal drum	6.50	.900	56	Moderate/Minor Rust
		Soln in outer polyethylene	6.60	.845	80	
		Soln inside polyethylene bag containing lead azide	6.90	.896	58	

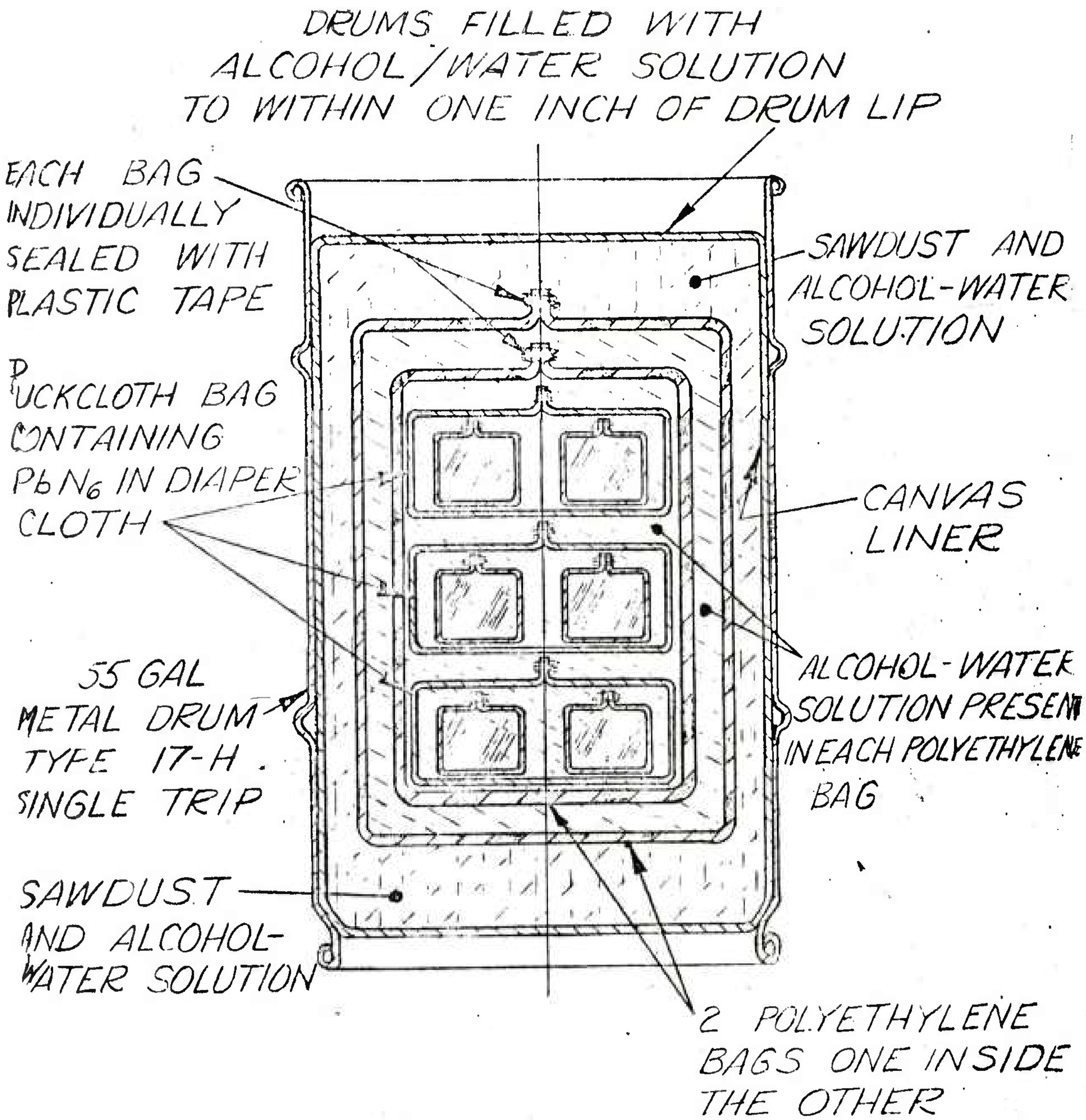

Fig 1 - DuPont Packaged Special Purpose Lead Azide

SAMPLES TAKEN FROM STORAGE DRUMS

FIGURE 2

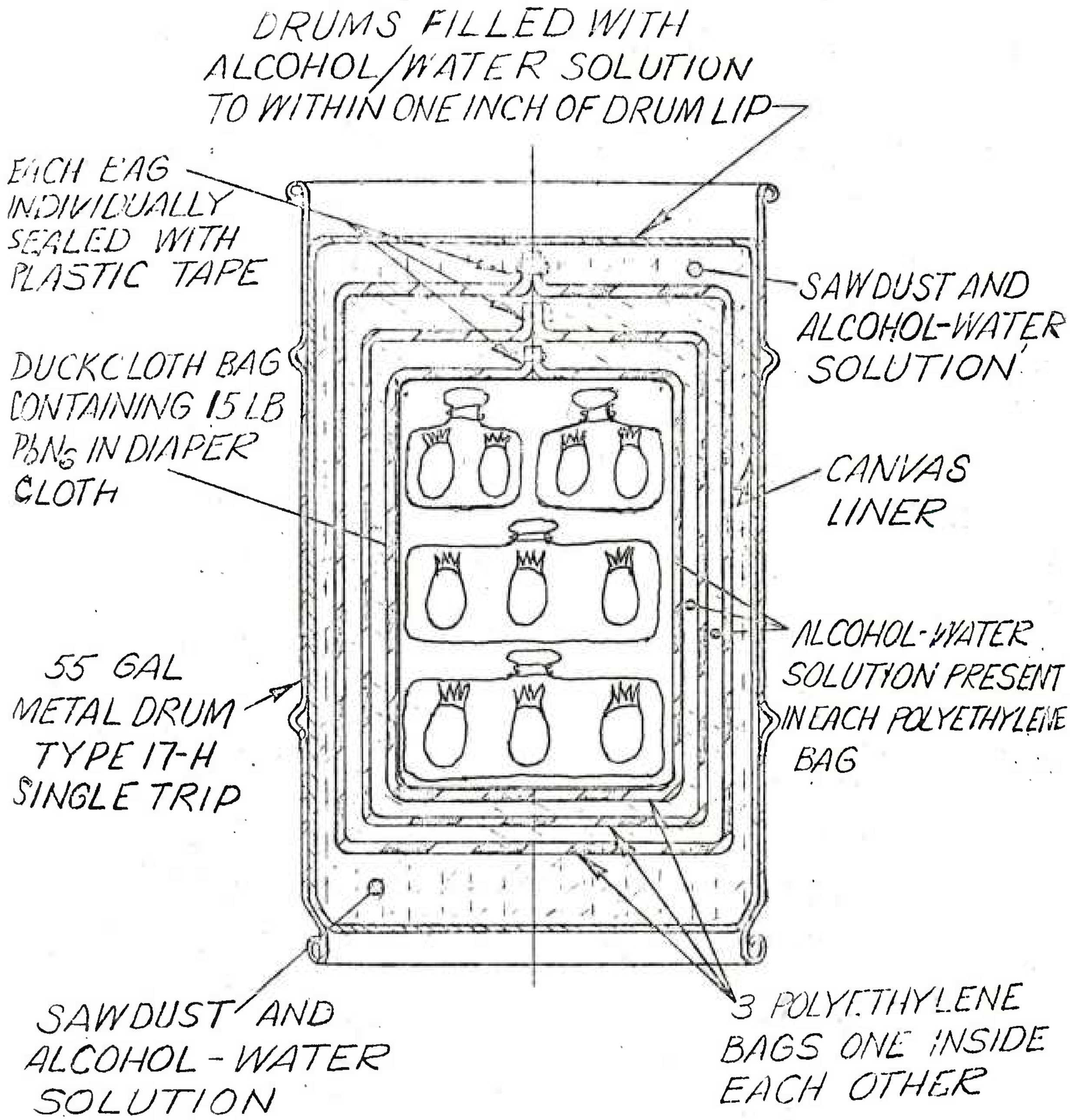

Fig 3 Uniroyal Packaged Special Purpose Lead Azide

SAMPLES TAKEN FROM STORAGE DRUMS

FIGURE 4

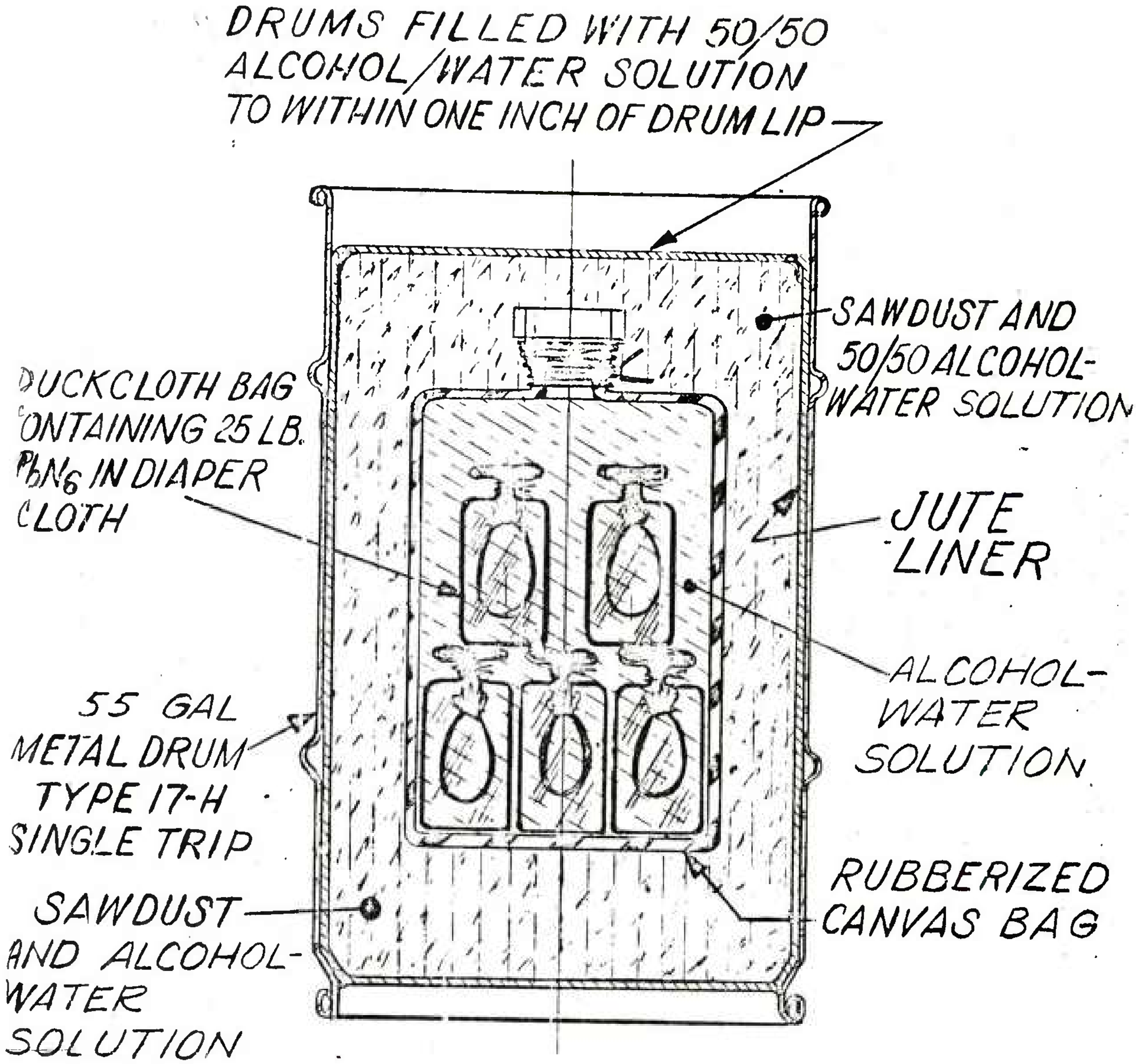

Fig 5 Olin Mathieson Packaged Special Purpose Lead Azide

SAMPLES TAKEN FROM STORAGE DRUMS

FIGURE 6

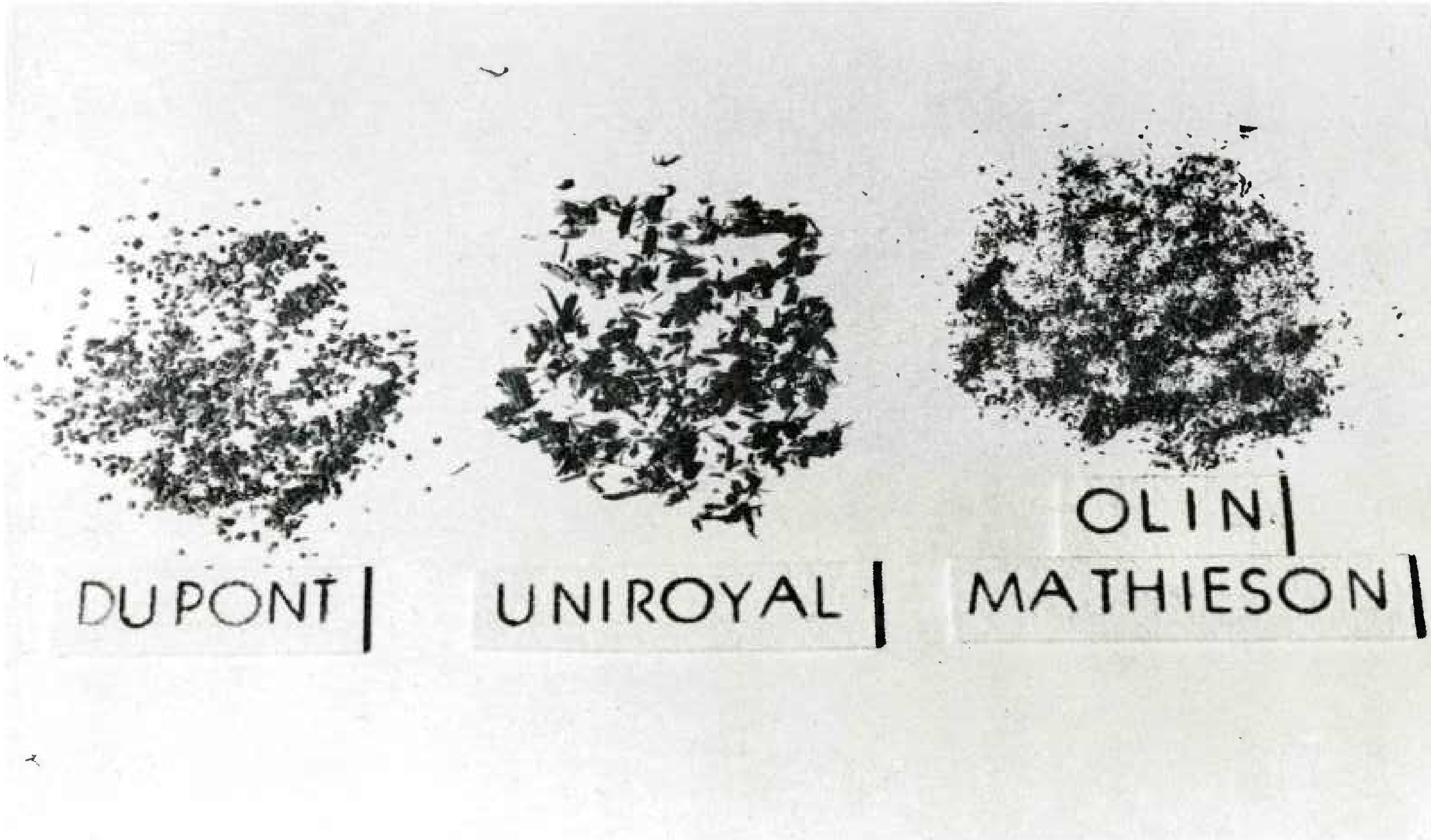

Fig 7 Sawdust Used by Various Manufacturers in Packaging Special Purpose Lead Azide

Appendix B

TRIP REPORT

LONG TERM STORAGE OF LEAD AZIDE

Savanna Ordnance Depot
Savanna, Illinois

Joseph Smith
15 May 1969

In continuing our studies on the effect of long term storage on special purpose lead azide, a trip was made to Savanna Ordnance Depot, Savanna, Illinois in order to inspect lead azide storage facilities and to become familiar with procedures used in packaging special purpose lead azide for storage.

Mr. Carl Schellinger and Mr. Leo Hillard of the Surveillance Directors Office coordinated this visit and supplied the necessary personnel to assist in the handling of the drums of lead azide selected for inspection. The surveillance team was under the direction of Mr. Ray Tryba.

Inspection of Lead Azide Storage Facilities:

The lead azide is stored in above-ground dome-shaped magazines which are covered with earth and seeded with grass. Magazines numbered E601, E615, and E616 were selected for inspection. Each magazine contains 156 drums of lead azide. The amount of lead azide in each drum on a dry weight basis (depending upon when the material was packaged) was either 125 pounds or 150 pounds.

The drums are stored in such a manner as to make each drum easily accessible for surveillance. A single row of 26 drums was aligned along each wall and two double rows containing 52 drums each was aligned along the center of the magazine. The distance between each row of drums is approximately 4 feet.

After the material was transported from Burlington, Iowa, to Savanna Ordnance Depot, each drum was opened and the liquid level of the 50/50 alcohol-water solution was checked. In most cases the liquid level was low, however, fresh alcohol-water solution was added to approximately one inch from the drum lip. The drum cover was then replaced by a modified cover which contains a small plexiglass viewing port approximately three inches in diameter. This viewing port facilitates the monitoring of the liquid inside the drum. This is only a storage cover and it is replaced with a standard cover when the drum is in transit.

Magazines are inspected monthly by a surveillance team and the liquid level in each drum is checked through the plexiglass viewing port, additional 50/50 alcohol-water solution is added as needed.

Housekeeping inside the magazine inspected was exceptional, no superfluous materials were detected and the dust level was at a minimum.

In the magazines inspected the liquid level in the lead azide

storage drums was clearly visible through the plexiglass viewing port, with the aid of a flashlight. Particularly striking was the range of colored liquids viewed; various shades of black, tan and wine colored solutions were observed. In some cases structural breakdown of the jute liner was clearly visible.

Temperature - humidity measurements are not recorded in each individual magazine, however, temperature data from a recorder located in an above-ground standard magazine is available.

Inspection of Drum Exterior:

Labeling on the exterior of the drums was clear and legible. The color of the drums varied with the manufacturer, in the magazines inspected drums containing DuPont material were white with black labeling, Uniroyal drums were olive green with yellow labeling and Olin drums were black with white labeling. In general the exterior of the drums does not show any gross signs of deterioration; only minor and incidental rust was observed.

On entering the storage magazines the odor of alcohol was very pronounced and on several of the drums inspected liquid leakage was observed around the plexiglass viewing port.

Inspection of Drum Interiors and Packaging Materials:

Permission was granted to open one drum of lead azide from each manufacturer. The purpose of opening the drums was to observe the interior condition of the drum and to inspect the packaging materials. Drums which have been in storage for the longest periods of time were selected to be opened for inspection. The drums of lead azide selected were removed from the magazine storage area and transported to a building located in a remote area where they were opened and unpacked.

No attempt was made to sample or inspect lead azide at this time, since recently 19 different lots of lead azide had been sampled by Savanna Ordnance Depot personnel and forwarded to Picatinny Arsenal for long term storage studies.

Drums from the following lot numbers were selected for inspection:

DuPont Lot #DUP-53-35 Drum #7 Manufacture Date 7/67
Uniroyal Lot #JA-4-50 Drum #34 Manufacture Date 6/67
Olin Lot #OLN-66-28 Drum #1 Manufacture Date 9/66

Visual inspection and observations during unpacking of selected drums were as follows:

The drums from the DuPont, Uniroyal and Olin manufactured lots contained 50/50 alcohol-water solution to within one inch of the drum lip. In all cases the 50/50 solution was black in color. The black liquid was siphoned off revealing a dark colored canvas bag in the DuPont and Uniroyal manufactured lot whereas the Olin manufactured lot contained a jute liner.

The canvas liner in both the DuPont and Uniroyal lots showed no signs of deterioration or structural weakness when tested by pulling and twisting. The top of the canvas bag contained sawdust which was black in color, however, approximately six inches down the sawdust had a brownish color. Several inches of sawdust was removed revealing a polyethylene bag sealed with black electrical tape.

The black electrical tape was used by all three manufacturers to seal the bags containing the lead azide. The tape was inspected by pulling and twisting and has maintained its structural integrity, however, very little, if any, of its adhesive properties remained.

The DuPont manufactured lot contained two polyethylene bags (one inside the other) each bag individually sealed with black electrical tape. Liquid was present in each polyethylene bag. The outer polyethylene bag contained brownish colored liquid whereas the inner bag which holds the lead azide contained a colorless liquid.

In all cases the interior of the drums from the lip to approximately a depth of 4 to 6 inches contained considerable rust. The rust easily flaked off when rubbed by the hand. However, below this level the interior walls of the drum were shiny and smooth. Drums used by all manufacturers are type 17H single trip metal drums and are not polyethylene coated.

The Uniroyal manufactured lot contained three polyethylene bags, one inside the other and each individually sealed with black electrical tape. Liquid was noted between each polyethylene bag. The outermost bag contained a black colored liquid, the middle bag contained a brownish colored liquid and the inner bag which holds the lead azide contained a colorless liquid.

In both the DuPont and Uniroyal manufactured lots the canvas cloth containing the lead azide and the polyethylene bags used showed no signs of deterioration or structural weakness.

The drum from the Olin manufactured lot contained a jute inner liner which showed some signs of deterioration and structural weakness of the fiber, however, the bag was still intact. The top of the liner contained sawdust which was black in color. After removal of considerable sawdust a single rubberized canvas bag sealed with black electric-

al tape was accessible. This bag contained the lead azide. From the depth of the bag inside the drum it would indicate considerable packing of the sawdust in the bottom of the jute liner had occurred.

The liquid inside the rubberized bag was slightly colored. The rubberized canvas bag and the canvas containing the lead azide showed no signs of structural weakness or deterioration.

Appendix C

TRIP REPORT

LONG TERM STORAGE OF LEAD AZIDE

Ravenna Army Ammunition Plant

Wayland, Ohio

Joseph Smith
12 June 1969

As part of our initial studies on the effect of long term storage on special purpose lead azide, it is necessary to become familiar with procedures used in packaging this material for storage. Preliminary inspection of special purpose lead azide stored at Savanna Ordnance Depot, showed that the material was packaged in a variety of ways. The DuPont and Uniroyal manufactured materials are packed in a similar manner, however, the Olin Mathieson material was packed quite differently.

Consequently, a trip was made to Ravenna Army Ammunition Plant, Wayland, Ohio, to observe the main storage facility for Olin Mathieson manufactured lead azide. Selected drums of special purpose lead azide were opened and unpacked to assess the condition of the drum interiors and to sample packaging materials.

Mr. J. DiMuro and Mr. C. Buterbaugh, RAI Contractor personnel, and Mr. P. Laro, AMC Property Officer, co-ordinated this visit and supplied the necessary personnel who assisted in the handling of the drums of lead azide selected for inspection. Handling and sampling procedures were cleared through Mr. G. Joyce, AMC Safety Officer.

Background:

During the month of March 1969, Ravenna Army Ammunition Plant received 781 drums containing 98,590 pounds of Special Purpose Lead Azide from Cornhusker Army Ammunition Plant. The greatest portion of this material (92,590 lbs) represented Olin Mathieson manufactured material, the remainder (6000 lbs) was material manufactured by DuPont. All material was manufactured and packaged in 1968. The Special Purpose Lead Azide has been in storage at Ravenna for a period of approximately three (3) months. The drums still contain the original shipping (transit) covers and they have not been opened since stored. Arrangements are underway to obtain storage covers which contain a plexiglass viewing port for monitoring the liquid level inside the drum. It is anticipated that the cover replacements will occur as soon as the materials become available. Presently the drums of Special Purpose Lead Azide are stored in six (6) igloos.

Inspection of Lead Azide Storage Facilities:

The lead azide is stored in above-ground dome-shaped storage igloos which are covered with earth and seeded with grass. Igloos numbered 2-D-2, 2-D-3, 2-D-4 and 2-D-6 were selected for inspection. Each igloo contains 144 drums of lead azide. The amount of lead azide in each drum depends upon the manufacturer; Olin Mathieson packs 125 pounds, whereas DuPont packs 150 pounds.

The drums are stored in such a manner as to make each drum

easily accessible for surveillance. Each igloo contained eight (8) double rows containing eighteen drums in each row. The storage drums are placed on 2x4 inch dunnage and the distance between drums is approximately six (6) to eight (8) inches. Aisles between double rows of drums are approximately four (4) feet wide.

Housekeeping inside the igloos inspected was satisfactory, no superfluous materials were observed and the dust level was at a minimum.

Temperature - humidity measurements are not recorded in each individual storage igloo, however, temperature data from a standard above ground igloo is available.

Inspection of Drum Exterior:

The color of the drums and labeling varied with the manufacturer. DuPont drums were white with black labeling and Olin Mathieson drums were black with white labeling. Labeling stenciled on the exterior of the drums was clear and legible. In general the exterior of the drums does not show any gross signs of deterioration; only minor and incidental rust was observed.

Inspection of Drum Interior and Packaging Materials:

Permission was granted to open six (6) drums of Special Purpose Lead Azide from representative lots in storage. The purpose of opening the drums was to observe the interior condition of the drum and to inspect the packaging materials. Five (5) drums from various Olin Mathieson manufactured lots were opened and inspected, one drum of which was selected from a lot shipped from Hercules Bacchus Works, Magna, Utah. Since a minimal quantity (6000 lb) of DuPont manufactured material is also stored at this location, one drum of this material was also selected for inspection. Drums of lead azide were opened and unpacked from the position they occupied in the storage igloo.

No attempt was made to sample lead azide at this time, since several lots of this material had previously been sampled while in storage at Cornhusker, and forwarded to Picatinny Arsenal for long term storage studies. However, in a few cases, bags containing the lead azide were opened to investigate the materials used in packaging and to assess the condition of these packaging materials.

Drums from the following lot numbers were selected for inspection:

Olin Mathieson, Lot # OM-1-17, Drum 63, Date Packed 2/68
Olin Mathieson, Lot # OM-1-19, Drum 9, Date Packed 2/68
Olin Mathieson, Lot # OM-1-22, Date Packed 4/68

Olin Mathieson, Lot # OM-1-24, Drum 29, Date Packed 5/68
Olin Mathieson, Lot # OM-1-15, Drum 32, Date Packed 1/68

(This lot shipped from Hercules Bacchus Works, Magna, Utah.)

DuPont, Lot # DUP-53-82, Drum 1, Date Packed 2/68

Visual inspection and observation during unpacking of selected drums were as follows:

The liquid level of the 50/50 water-alcohol solution in the Olin Mathieson and DuPont Manufactured lots was approximately one (1) to three (3) inches from the lip of the drum and the color of the liquid varied from brownish - yellow to black.

The liquid was siphoned off revealing a jute liner in the Olin manufactured lots, whereas the DuPont manufactured lot contained a canvas liner. All liners were sewn and completely intact, fibers showed no visible signs of deterioration or structural weakness.

On opening the liner, in most cases the sawdust packing was exposed, however, in two cases, Lot # OM-1-15 and Lot # OM-1-22, the sawdust was of very fine particle size which had packed and settled considerably and upon opening the jute liner the rubberized canvas bag was exposed, no top sawdust packing was present in the drums inspected. In all cases the layer of sawdust next to the liner was black in color, however, beyond this layer the sawdust was brownish in color and showed no signs of deterioration.

After removing several inches of sawdust from the liner a rubberized canvas bag was exposed in the Olin manufactured lot, whereas, the DuPont lot contained a polyethylene bag.

In the Olin manufactured lots the top of the rubberized canvas bag was folded over and secured with cotton cord. In all drums inspected the rubberized bag was opened and the 50/50 water-alcohol solution varied in color from light yellow to yellowish brown. The bag contained five (5) packages, each containing twenty-five (25) pounds of lead azide. One of the packages of lead azide was opened and unpacked for inspection of packaging materials. The lead azide was contained in a square diaper cloth, the ends drawn up and secured with cotton cord, this in turn was contained in a single duck canvas bag, which was secured with cotton cord. Each package was identified by a paper tag which was secured to the duck canvas bag. This tag contained the manufacturer's lot number, date material was packed and the weight of lead azide. All fabric materials showed good structural strength and no signs of deterioration were noted.

In the DuPont manufactured lot the lead azide was contained in two (2) polyethylene bags (one inside the other), each bag individually sealed with black plastic tape. Alcohol-water solution was contained in each polyethylene bag. The outer polyethylene bag contained a yellowish-brown colored liquid whereas the inner bag (which contains the lead azide) contained a colorless liquid. The lead azide was contained in a square diaper cloth, the ends drawn up and secured with cotton cord. Each package of lead azide was identified with both a black rubber tag and a paper tag containing the batch number. Two (2) of these packages were contained in a single bag of diaper cloth which was secured with cotton cord. The batch numbers in the bag opened were No. 15194 and No. 15195. All fabric and polyethylene materials showed good structural strength and no signs of deterioration were noted, however, the black plastic tape peeled off with very little effort and retained very little if any adhesive property.

In all cases the interior of the lids and drums showed minor to moderate conditions of rust. Drums used by both manufacturers are type 17-H single trip metal drums and are not polyethylene coated.

Appendix D

TRIP REPORT

LONG TERM STORAGE OF LEAD AZIDE

Joliet Army Ammunition Plant
Joliet, Illinois

Joseph R. Smith
31 July 1970

From July 27 - 31, a representative of the Explosives Division visited Joliet Army Ammunition Plant. The purpose of this visit was to obtain new storage samples of special purpose lead azide for long term storage studies. Lead azide stored at Joliet, was manufactured and packaged by Uniroyal contract personnel in 1968.

Mr. Valerio (COR), Quality Assurance Division, coordinated this visit and Messrs. Hicke, Baggett, Orlomoski, Uniroyal contractor personnel, assisted in the sampling of the lead azide.

Drums from eight different lots of special purpose lead azide were randomly selected for sampling. In addition to sampling the lead azide, all alcohol-water solutions present inside the storage drums were carefully sampled. All samples will be shipped to the Explosives Division for testing and evaluation.

During the unpackaging operation the following observations were noted:

<u>Drum Interior</u>:

The liquid level of the alcohol-water solution inside the storage drums was approximately two to four inches from the top of the drum lip. Storage lids which contain a threaded plexiglass viewing port for monitoring the liquid level inside the drums were installed in November 1969. Drum lids (interior) show some signs of incidental rust. The foam rubber gaskets used to seal the lids show good physical properties.

The interior of the drums was examined to a depth of approximately 18 inches; no rust, scale or pitting of the metal surface was observed. The drum interiors are coated with a red phenolic coating which does not show any visual signs of deterioration.

<u>Drum Exterior</u>:

All markings and/or labeling on the exterior of the drums were clear and legible. In general the exterior of the drums selected for sampling did not show any gross signs of deterioration; in one case only incidental rust was observed around the bottom seam of the drum.

<u>Packaging Materials</u>:

No visual signs of deterioration or structural weakness were detected in packaging materials such as Osnaburg drum liner, sawdust, polyethylene bags, duck cloth and diaper cloth. However, the black plastic tape used in securing the polyethylene bags does show a

definite loss of adhesive properties. In one case it was observed that the black plastic tape used to secure the outermost polyethylene bag had come loose, allowing liquid to enter the bag.

DRUM INTERIOR - VISUAL INSPECTION

UNIROYAL (Mfg. date 1968)	CONDITION OF STORAGE LID*	CONDITION OF DRUM INTERIOR**
Lot # JA-4-76	Incidental Rust - Gasket Good	No indications of any rust or scale
Lot # JA-4-80	Incidental Rust - Gasket Good	No indications of any rust or scale
Lot # JA-4-82	Incidental Rust - Gasket Good	No indications of any rust or scale
Lot # JA-4-86	No Evidence of Rust - Gasket Good	No indications of any rust or scale
Lot # JA-4-88	Incidental Rust - Gasket Good	No indications of any rust or scale
Lot # JA-4-85	Incidental Rust - Gasket Good	No indications of any rust or scale
Lot # JA-4-91	Incidental Rust - Gasket Good	No indications of any rust or scale
Lot # JA-4-95	Incidental Rust - Gasket Good	No indications of any rust or scale

* New storage lids with foam rubber gasketing installed in Nov. 1969.

** Drum interior coated with a phenolic (red) coating.

DRUM EXTERIOR - VISUAL INSPECTION

UNIROYAL (Mfg. date 1968)	DRUM MARKINGS	CONDITION OF DRUM EXTERIOR
Lot # JA-4-76	Clear, Legible	No evidence of rust around bottom seam
Lot # JA-4-80	Clear, Legible	No evidence of rust around bottom seam
Lot # JA-4-82	Clear, Legible	No evidence of rust around bottom seam
Lot # JA-4-86	Clear, Legible	No evidence of rust around bottom seam
Lot # JA-4-88	Clear, Legible	Incidental rust around bottom seam
Lot # JA-4-85	Clear, Legible	No evidence of rust around bottom seam
Lot # JA-4-91	Clear, Legible	No evidence of rust around bottom seam
Lot # JA-4-95	Clear, Legible	No evidence of rust around bottom seam

PACKAGING MATERIALS IN CONTACT WITH LEAD AZIDE

UNIROYAL (Mfg. date 1968)	Color of Alcohol-Water Solution	Condition of Duck Cloth Bag	Condition of Diaper Cloth
Lot # JA-4-76	Colorless	Good	Good, no residue or stains
Lot # JA-4-80	Pink	Good	Good, reddish colored stains
Lot # JA-4-82	Colorless	Good	Good, no residue or stains
Lot # JA-4-86	Colorless	Good	Good, no residue or stains
Lot # JA-4-88	Colorless	Good	Good, no residue or stains
Lot # JA-4-85	Slight dis-coloration	Good	Good, no residue or stains
Lot # JA-4-91	Colorless	Good	Good, no residue or stains
Lot # JA-4-95*	Pinkish/red	Good	Reddish color stains

*During the unpackaging of Uniroyal Lot # JA-4-95 it was observed that the black plastic tape on the outermost polyethylene bag had lost its adhesive properties. The tape came loose, allowing liquid to enter the polyethylene bag.

PACKAGING MATERIALS IN CONTACT WITH DRUM

UNIROYAL (Mfg. date 1968)	Color of Alcohol-Water Solution*	Type and Condition of Drum Liner**	Sawdust
Lot #JA-4-76	Reddish	Osnaburg, good	Top layer - 2-4" deep
Lot #JA-4-80	Reddish	Osnaburg, good	Top layer - 4-6" deep
Lot #JA-4-82	Reddish	Osnaburg, good	Top layer - 2-4" deep
Lot #JA-4-86	Reddish	Osnaburg, good	Top layer - 2-4" deep
Lot #JA-4-88	Reddish	Osnaburg, good	Top layer - 2-4" deep
Lot #JA-4-85	Reddish	Osnaburg, good	Top layer - 4-6" deep
Lot #JA-4-91	Reddish	Osnaburg, good	Top layer - 4-6" deep
Lot #JA-4-95	Reddish	Osnaburg, good	Top layer - 2-4" deep

* Alcohol-Water solution - Liquid level approximately 2 to 4 inches from the top of the drum lip.

** Osnaburg drum liner - A type of coarse, heavy cloth made of cotton.

EXIT TRIP REPORT
JOLIET ARMY AMMUNITION PLANT
JOLIET, ILLINOIS 60436

Date: 31 July 1970

Name: Joseph R. Smith

Organization and
Address: Explosive Division (FRL), Picatinny Arsenal, Dover, N.J.

Dates of Visit: 27 - 31 July 1970

Purpose of Visit: To sample various lots of Special Purpose Lead Azide

Personnel Contacted: Mr. Valerio (COR); Mr. Hicke, Mr. Baggett, Mr. Orlomoski, Mr. Paganoni (Uniroyal Personnel)

Observations and Findings: Drum from eight different lots of Special Purpose lead Azide manufactured and packaged by Uniroyal were randomly selected for sampling. During the unpackaging and sampling operation the following observations were made:

Drum Exterior: In general the exterior of the drums didn't show any gross signs of deterioration, in a few cases incidental rust was observed around the bottom seam of the drum.

Drum Interior: The liquid level of the alcohol-water solution inside the drums was approximately 3-4 inches from the top of the drum lip.

The interior of the drum was examined to a depth of approximately 18 inches; no rust, scale or pitting of the surface was observed. The phenolic coating on the inside of the drum does not show any visual signs of deterioration. In a few cases some rust was observed on the drum top (area under the lid gasket).

No visual signs of deterioration or structural weakness was detected in packaging materials such as drum liners, sawdust, polyethylene bags, duck cloth and diaper cloth. However, the black plastic tape used in securing the polyethylene bags did show a definite loss (breakdown) of adhesive properties.

Recommendations: Samples of lead azide and alcohol-water solutions will be returned to Picatinny Arsenal for testing and evaluation. No recommendations can be made at this time. Special thanks to the above named personnel for making my visit pleasant and successful.

Appendix E

TRIP REPORT

LONG TERM STORAGE OF LEAD AZIDE

Savanna Army Depot
Savanna, Illinois

Joseph R. Smith
June 15, 1970

On 9 February 1970 a Board was established to examine and make recommendations on the Munitions Command (MUCOM) position concerning the Long Term Storage of lead azide. At the second Board Meeting held in April 1970, it was suggested that new storage samples be obtained for testing. Accordingly, a representative (Mr. Joseph Smith) of the Explosives Division visited the Savanna Army depot on June 15 - 19 in order to sample seventeen (17) different lots of special purpose lead azide.

Mr. Jack Lancaster and Mr. Don Keller of the Surveillance Directors Office coordinated this visit and supplied the necessary personnel to assist in handling the drums of lead azide selected for sampling.

Drums from seventeen (17) different lots of Special Purpose Lead Azide (SPLA) were randomly selected for sampling. In addition to sampling the lead azide, all alcohol-water solutions present inside the storage drums were also carefully sampled. All samples will be shipped to the Explosives Division for testing and evaluation.

Two drums containing Olin Mathieson lots manufactured in 1966 and 1967 were selected by Savanna personnel and identified as examples of storage drums which show poor exterior conditions (worst possible cases). The lead azide was removed and the drums along with all packaging materials were also shipped to Picatinny Arsenal for evaluation.

During the unpackaging operation the following observations were made:

Drum Interior

Storage drums are provided with removable covers (lids) which contain a foam rubber gasketing material. The cover is secured to the drum by means of a bolted locking ring. Drums used by all manufacturers are type 17H single trip metal drums made from low carbon, open-hearth or electric cold rolled steel.

The liquid level of the alcohol-water solution inside the storage drums varied within 1 to 3 inches from the top of the drum lip. Storage lids of all drums sampled show signs of incidental to moderate rust and/or scale. In most cases, the foam rubber gasketing materials has deteriorated to the point where it no longer provides an adequate seal.

Drum interiors of materials packaged by Uniroyal show little or no evidence of rust and/or scale. DuPont packaged materials show minor to moderate rust and/or scale to a depth of 2 to 6 inches; below this level the drum surface is smooth and shiny. Olin Mathieson

packaged materials show major rust and/or scale which easily flaked off. The average depth varied from 4 to 10 inches (and in one case to a depth of 24 inches); below this level the drum surface is smooth and shiny.

Drum Exterior

All markings and/or labeling on the exterior of the drums packaged by DuPont and Uniroyal were clear and legible. Of the six drums of Olin Mathieson packaged material selected for sampling, three drums had faded and/or blurred markings which were difficult to read, markings on the other three drums were clear and legible.

In general, the exterior of all drums selected for sampling did not show any gross signs of deterioration, only incidental to minor rust was observed around the bottom seam of the drum. Olin Lot #66-27 and 67-17 were selected by Savanna personnel and identified as examples of storage drums which show poor exterior conditions (worst possible condition).

Packaging Materials

All packaging materials such as jute drum liners, canvas drum liners, rubberized canvas bags, polyethylene bags, diaper cloth and duck cloth show no visual signs of deterioration or structural weakness.

Both Uniroyal and DuPont packaged materials contained a top cushioning layer of sawdust which averaged 4 to 6 inches deep. The Olin Mathieson packaged material had no top cushioning layer of sawdust. The sawdust has settled and/or packed to the point where the top of the rubberized bag is exposed.

DRUM EXTERIOR - VISUAL INSPECTION

	Drum Markings	Condition of Drum Exterior
Olin Mathieson (Mfg date 1967)		
*Lot #Olin 66-27	Clear	Drum dented around top & bottom Minor rust around bottom seam
Lot #Olin 66-28	Faded, difficult to read	Drum dented around top & bottom Minor rust around bottom seam
Lot #Olin 66-31	Clear, Legible	Drum dented around top & bottom Minor rust around bottom seam
Olin Mathieson (Mfg date 1968)		
Olin Lot #67-3	Faded, blurred, difficult to read	Drum dented around top & bottom Minor rust around bottom seam
Olin Lot #67-8	Legible	Incidental rust around bottom seam
*Olin Lot #67-17	Faded, difficult to read	Drum dented around top & bottom Minor rust around bottom seam
Uniroyal (Mfg date 1967)		
Lot # JA 4-55	Clear, Legible	Incidental rust around bottom seam
Lot # JA 4-71	Clear, Legible	No evidence of rust
Dupont (Mfg date 1967)		
Lot # Dup 53-20	Clear, Legible	Minor rust around bottom seam
Lot # Dup 53-24	Clear, Legible	Minor rust around bottom seam
Lot # Dup 53-30	Clear, Legible	Minor rust around bottom seam
Lot # Dup 53-36	Clear, Legible	Incidental rust around bottom seam
Lot # Dup 53-41	Clear, Legible	Minor rust around bottom seam
Lot # Dup 53-49	Clear, Legible	Minor rust around bottom seam
Lot # Dup 53-49	Clear, Legible	Minor rust around bottom seam
Lot # Dup 53-54	Clear, Legible	Incidental rust around bottom seam
Lot # Dup 53-72	Clear, Legible	Incidental rust around bottom seam
Dupont (Mfg date 1968)		
Lot # Dup 53-91	Clear, Legible	Minor rust around bottom seam

* Drums selected by Savanna personnel and identified as examples of storage drums which show poor exterior conditions.

DRUM INTERIOR - VISUAL INSPECTION

	Condition of Storage Lid*	Condition of Drum Interior**
Olin Mathieson (Mfg date 1966)		
Lot # Olin 66-27	Moderate Rust-Gasket Deterioration	Major rust and/or scale depth of 4-6 inches
Lot # Olin 66-28	Moderate Rust-Gasket Deterioration	Major rust and/or scale depth of 8-10 inches
Lot # Olin 66-31	Moderate Rust-Gasket Deterioration	Major rust and/or scale depth of 4-6 inches
Olin Mathieson (Mfg date 1967)		
Lot # Olin 67-3	Moderate Rust-Gasket Deterioration	Major rust and/or scale depth of 24 inches
Lot # Olin 67-8	Minor Rust-Gasket Deterioration	Major rust and/or scale depth of 6-8 inches
Lot # Olin 67-17	Moderate Rust-Gasket Deterioration	Major rust and/or scale depth of 6-8 inches
Uniroyal (Mfg date 1967)		
Lot # JA 4-55	Incidental Rust-Gasket Good	Incidental rust
Lot # JA 4-71	Incidental Rust-Gasket Good	No evidence of rust
Dupont (Mfg date 1967)		
Lot # Dup 53-20	Minor rust-Gasket deterioration	Minor to moderate rust depth of 2-4 inches
Lot # Dup 53-24	Incidental rust-Gasket deterioration	Moderate rust and/or scale depth of 4-6 inches
Lot # Dup 53-30	Minor rust-Gasket deterioration	Moderate rust and/or scale depth of 4-6 inches
Lot # Dup 53-36	Minor rust-Gasket deterioration	Moderate rust and/or scale depth of 4-6 inches
Lot # Dup 53-41	Incidental rust-Gasket good	Moderate rust and/or scale depth of 4-6 inches
Lot # Dup 53-49	Incidental rust-Gasket good	Minor rust and/or scale depth of 2-4 inches
Lot # Dup 53-54	Incidental rust-Gasket good	Minor rust and/or scale depth of 2-4 inches
Lot # Dup 53-72	Incidental rust-Gasket good	Minor rust and/or scale depth of 2-4 inches
Dupont (Mfg date 1968)		
Lot # Dup 53-91	Incidental rust-Gasket good	Minor rust and/or scale depth of 2-4 inches

* Gasket deterioration - No physical strength or resiliency - no longer provides an adequate seal.
** Below this level, drum surface is smooth and shiny

PACKAGING MATERIALS IN CONTACT WITH DRUM

	Color of Alcohol-Water Solution*	Type and Condition of Drum Liner	Sawdust**
Olin Mathieson (Mfg date 1966)			
Lot #Olin 66-27	Black	Jute, good, top sewed	No top layer - settled
Lot #Olin 66-28	Rusty	Jute, good, top sewed	No top layer - settled
Lot #Olin 66-31	Black	Jute, good, top sewed	No top layer - settled
Olin Mathieson (Mfg date 1967)			
Lot #Olin 67-3	Black	Jute, good, top sewed	No top layer - settled
Lot #Olin 67-8	Black	Jute, good, top sewed	No top layer - settled
Lot #Olin 67-17	Black	Jute, good, top sewed	No top layer - settled
Uniroyal (Mfg date 1967)			
Lot # JA 4-55	Reddish	Canvas, good, top sewed	Top layer 4-6" deep
Lot # JA 4-71	Reddish	Canvas, good, top sewed	Top layer 4-6" deep
Dupont (Mfg date 1967)			
Lot #Dup 53-20	Brown	Canvas, good, top sewed	Top layer 4-6" deep
Lot #Dup 53-24	Black	Canvas, good, top sewed	Top layer 4-6" deep
Lot #Dup 53-30	Brown	Canvas, good, top sewed	Top layer 4-6" deep
Lot #Dup 53-36	Black	Canvas, good, top sewed	Top layer 4-6" deep
Lot #Dup 53-41	Black	Canvas, good, top sewed	Top layer 4-6" deep
Lot #Dup 53-49	Black	Canvas, good, top sewed	Top layer 4-6" deep
Lot #Dup 53-54	Brown	Canvas, good, top sewed	Top layer 4-6" deep
Lot #Dup 53-72	Brown	Canvas, good, top sewed	Top layer 4-6" deep
Dupont (Mfg date 1968)			
Lot #Dup 53-91	Reddish Brown	Canvas, good, top sewed	Top layer 4-6" deep

* Alcohol-Water solution - Liquid level approximately 1 to 3 inches from top of drum lid.

** No top layer of sawdust - packing and/or settling of the sawdust has occurred to the point where there is no longer any top cushioning layer of sawdust.

PACKAGING MATERIALS IN CONTACT WITH LEAD AZIDE

	Color of Alcohol-Water Solution	Condition of Duck Cloth Bag	Condition of Diaper Cloth
Olin Mathieson (Mfg date 1966)			
Lot #Olin 66-27	Brownish	Good	Good
Lot #Olin 66-28	Slight Coloration	Good	Good
Lot #Olin 66-31	Brown	Good	Good, Heavy accumulation of brownish color residue
Olin Mathieson (Mfg date 1967)			
Lot #Olin 67-3	Reddish-Brown	Good	Good
Lot #Olin 67-8	Slight Coloration	Good	Good
Lot #Olin 67-17	Brown	Good	Good, heavy deposits of brown colored residue
Uniroyal (Mfg date 1967)			
Lot #JA 4-55	Colorless	Good	Good
Lot #JA 4-71	Colorless	Good	Good
Dupont (Mfg date 1967)			
Lot #Dup 53-20	Colorless	Good	Good
Lot #Dup 53-24	Colorless	Good	Good
Lot #Dup 53-30	Colorless	Good	Good
Lot #Dup 53-36	Colorless	Good	Good
Lot #Dup 53-41	Colorless	Good	Good
Lot #Dup 53-49	Colorless	Good	Good
Lot #Dup 53-54	Colorless	Good	Good
Lot #Dup 53-72	Colorless	Good	Good
Dupont (Mfg date 1968)			
Lot #Dup 53-91	Colorless	Good	Good

Appendix F

TRIP REPORT

LONG TERM STORAGE OF LEAD AZIDE
Ravenna Army Ammunition Plant

Joseph R. Smith
July 17, 1970

On July 14 - 17 a representative of the Explosives Division visited Ravenna Army Ammunition Plant, the main storage facility for Olin Mathieson manufactured lead azide. The purpose of this visit was to continue collecting storage samples of Special Purpose Lead Azide for long term storage studies.

During March 1969, Ravenna received 781 drums containing 98,590 pounds of Special Purpose Lead Azide from Cornhusker Army Ammunition Plant. The greatest part of this material (92,590 lbs) was manufactured by Olin Mathieson, the remaining 6000 lbs was manufactured by Dupont. All material was manufactured and packaged in 1968.

Mr. Dave Emerson and Mr. David Wenzel, COR personnel, coordinated this visit. Mr. Carl Buterbough, RAI contractor personnel, supplied the necessary personnel to assist in handling the drums of lead azide selected for sampling.

Drums from thirteen (13) different lots of special purpose lead azide (SPLA) were randomly selected for sampling. In addition to sampling the lead azide, all alcohol-water solutions present inside the storage drums were carefully sampled. All samples will be shipped to the Explosives Division for testing and evaluation.

During the unpackaging operation the following observations were noted:

Drum Interior

Storage drums are provided with removable covers (lids) which contain a foam rubber gasket. The cover is secured to the drum by means of a bolted locking ring. As reported in trip report dated 12 June 1969, drums still contain the original shipping (transit) covers. Storage covers which contain a plexiglass viewing port for monitoring the liquid level inside the drums still have not been installed.

The liquid level of the alcohol-water solution inside the storage drums was approximately two to six inches from the top of the drum lip. Drum lids (interiors) showed signs of incidental to moderate conditions of rust and/or scale. The foam rubber gasketing material on the Olin Mathieson packaged material was generally fair to good (in a few cases some deterioration was noted) whereas the black rubber (Neoprene) gasketing used by Dupont was in excellent condition.

Drum interiors of Olin Mathieson manufactured and packaged materials in most cases show incidental to minor rust and/or scale to a depth of three to eight inches. (In three cases the condition was classified as moderate rust). Below this level the interior walls of the drum were shiny and smooth. Drums containing Dupont package

materials show no evidence of rust, however, some pitting of the metal surface was noted.

Drum Exterior:

All markings and/or labeling on the exterior of the drums were clear and legible. In general the exterior of the drums selected for sampling did not show any gross signs of deterioration; only incidental to minor rust was observed around the bottom seam of the drum.

Packaging Materials:

Packaging materials such as jute drum liners, canvas drum liners, rubberized canvas bags, polyethylene bags, diaper cloth and duck cloth show good structural strength and no visual signs of deterioration was noted. Black plastic tape used by Dupont to seal polyethylene bags shows loss of adhesive properties.

Dupont packaged material contained a top cushioning layer of sawdust which averaged four to six inches deep. Olin Mathieson packaged material had no top cushioning layer of sawdust. The sawdust has settled and/or packed to the point where the top of the rubberized bag is exposed.

DRUM INTERIOR - VISUAL INSPECTION

OLIN MATHIESON (Mfg. date 1968)	Condition of Storage Lid	Condition of Drum Interior*
Lot #OLIN 1-15	Coated with black residue	Coated with black residue
Lot #OLIN 1-16	Incidental rust-gasket good	
Lot #OLIN 1-17	Incidental rust-gasket good	Incidental rust around drum lip
Lot #OLIN 1-18	Incidental rust-gasket good	Incidental rust and/or scale depth of 3 inches
Lot #OLIN 1-19	Incidental rust-gasket good	Incidental rust and/or scale depth of 3 inches
Lot #OLIN 1-20	Minor pitting - gasket good	Minor pitting, drum surface shiny
Lot #OLIN 1-21	Minor rust - gasket good	Minor/moderate rust depth of 6-8 inches
Lot #OLIN 1-22	Minor rust - gasket fair	Minor rust and/or scale depth of 4 inches
Lot #OLIN 1-23	Minor rust - gasket good	Minor rust and/or scale depth of 4-6 inches
Lot #OLIN 1-24	Moderate rust - gasket good	Moderate rust and/or scale depth of 4-6 inches
Lot #OLIN 1-25	Moderate rust - gasket fair	Moderate rust and/or scale depth of 4-6 inches

DUPONT (Mfg. date 1968)		
Lot #DUP 53-82	Incidental rust - gasket excellent**	Incidental pitting and/or scale
Lot #DUP 53-83	Incidental rust - gasket excellent**	Incidental pitting and/or scale

* Below this level the drum surface is smooth and shiny; black residue easily rubs off, surface underneath is smooth and shiny.

** Gasketing used on Dupont Storage Lid is black rubber (Neoprene)
Gasketing used on Olin Storage Lid is foam rubber type.

DRUM EXTERIOR - VISUAL INSPECTION

OLIN MATHIESON (Mfg. date 1968)	DRUM MARKINGS	CONDITION OF DRUM EXTERIOR
Lot #OLIN 1-15	Clear, Legible	Incidental rust around bottom seam
Lot #OLIN 1-16	Clear, Legible	Incidental rust around bottom seam
Lot #OLIN 1-17	Clear, Legible	Incidental rust around bottom seam
Lot #OLIN 1-18	Clear, Legible	Incidental rust around bottom seam
Lot #OLIN 1-19	Clear, Legible	Incidental rust around bottom seam
Lot #OLIN 1-20	Clear, Legible	Minor rust around bottom seam
Lot #OLIN 1-21	Clear, Legible	Incidental rust around bottom seam
Lot #OLIN 1-22	Clear, Legible	Minor rust around bottom seam
Lot #OLIN 1-23	Clear, Legible	Minor rust around bottom seam
Lot #OLIN 1-24	Clear, Legible	Incidental rust around bottom seam
Lot #OLIN 1-25	Clear, Legible	Incidental rust around bottom seam
DUPONT (Mfg. date 1968)		
Lot #DUP 53-82	Clear, Legible	Incidental rust around bottom seam
Lot #DUP 53-83	Clear, Legible	Incidental rust around bottom seam

PACKAGING MATERIALS IN CONTACT WITH LEAD AZIDE

OLIN MATHIESON (Mfg. date 1968)	Color of Alcohol-Water Solution	Condition of Duck Cloth Bag	Condition of Diaper Cloth
Lot #OLIN 1-15	Brown	Good	Good, stained with brown residue
Lot #OLIN 1-16*	Black	Good	Good, stained with black residue
Lot #OLIN 1-17	Brown	Good	Good, stained with reddish residue
Lot #OLIN 1-18	Brown	Good	Good, stained with reddish residue
Lot #OLIN 1-19	Brown	Good	Good, stained with reddish residue
Lot #OLIN 1-20	Brown	Good	Good, stained with brown residue
Lot #OLIN 1-21	Brown	Good	Good, no residue or stains
Lot #OLIN 1-22	Brown	Good	Good, stained with reddish residue
Lot #OLIN 1-23	Brown	Good	Good, stained with brown residue
Lot #OLIN 1-24	Brown	Good	Good, no residue or stains
Lot #OLIN 1-25	Brown	Good	Good, no residue or stains
DUPONT (Mfg. date 1968)			
Lot #DUP 53-82	Colorless	Good	Good, no residue or stains
Lot #DUP 53-83	Colorless	Good	Good, no residue or stains

*During the unpackaging of Olin Mathieson lot 1-16 BBL #14 it was observed that the jute drum liner was not sewn closed and the rubberized bag containing the lead azide was opened.

PACKAGING MATERIALS IN CONTACT WITH DRUM

OLIN MATHIESON (Mfg. date 1968)	Color of Alcohol-Water Solution	Type and Condition of Drum Liner	Sawdust**
Lot #OLIN 1-15	Black	Jute, good, top sewed	No top layer - settled
Lot #OLIN 1-16	Black	Jute, good, top opened	No top layer - settled
Lot #OLIN 1-17	Black	Jute, good, top sewed	No top layer - settled
Lot #OLIN 1-18	Black	Jute, good, top sewed	Top layer 2 inches deep
Lot #OLIN 1-19	Brown	Jute, good, top sewed	Top layer 4-6 inches deep
Lot #OLIN 1-20	Black	Jute, good, top sewed	No top layer - settled
Lot #OLIN 1-21	Black	Jute, good, top sewed	No top layer - settled
Lot #OLIN 1-22	Black	Jute, good, top sewed	No top layer - settled
Lot #OLIN 1-23	Black	Jute, good, top sewed	No top layer - settled
Lot #OLIN 1-24	Black	Jute, good, top sewed	No top layer - settled
Lot #OLIN 1-25	Black	Jute, good, top sewed	Top layer 2 inches deep
DUPONT (Mfg. date 1968)			
Lot #DUP 53-82	Reddish	Canvas, good, top sewed	Top layer 4-6 inches deep
Lot #DUP 53-83	Black	Canvas, good, top sewed	Top layer 4-6 inches deep

* Alcohol-Water solution - Liquid level approximately 2 to 6 inches from top of drum lip.

** No top layer of sawdust - Packing and/or settling of the sawdust has occurred to the point where there is no longer any top cushioning layer of sawdust.

Appendix G

TRIP REPORT

SPECIAL PURPOSE LEAD AZIDE

SURVEILLANCE STUDIES

Joliet Army Ammunition Plant
Joliet, Illinois

Joseph R. Smith
July 11-17, 1971

From July 11-17, a representative of the Explosives Division visited Joliet Army Ammunition Plant. The purpose of this visit was to obtain samples of Special Purpose Lead Azide in order to continue long term storage surveillance studies. Lead Azide stored at Joliet, was manufactured and packaged by Uniroyal during 1967 and 1968.

Mr. J. White (COR), Quality Assurance Division, coordinated this visit and Messrs. Hicke, Delpierre, Orlomoski, Olmeted, Brandolino, Uniroyal contractor personnel, assisted in the sampling of the lead azide. Funding for the sampling operations was provided by Picatinny Arsenal.

Drums from sixteen (16) different lots of Special Purpose Lead Azide were randomly selected for sampling. In addition to sampling the lead azide, all alcohol-water solutions present inside the storage drums were carefully sampled. All samples were shipped to the Explosives Division for testing and evaluation.

During the sampling operation the following observations were noted:

Packaging Configuration:

The Uniroyal packaged lead azide contained three polyethylene bags one inside the other and each individually sealed with black plastic tape. The lead azide (15 lb batch) is contained in a diaper cloth, with the ends pulled together and tied with cotton cord. Each batch is tagged with a rubber tag containing the batch number. Ten batches (150 lbs) of lead azide are packaged into four duck cloth bags, each secured with cotton cord. The four bags are packaged in the innermost polyethylene bag which contains sufficient ethyl alcohol to keep the bags submerged.

Each fifty-five gallon drum is lined with an Osnaburg liner. The bottom of the liner contains 4 to 6 inches of sawdust which acts as a cushioning medium. The polyethylene bags containing the azide is placed on the sawdust cushion and the bag is covered with 4 to 6 inches of sawdust. The top of the liner is sewed in order to keep the packaging configuration together. The drum is then filled with alcohol-water solution to within 1 to 2 inches from the drum lip.

During storage the drum is covered with a strong lid which contains a plexiglass viewing port for monitoring the liquid level inside the drum. The lid contains a foam rubber gasket and is secured to the drum by means of a bolted locking ring.

Drum Exterior:

All markings and/or labeling on the exterior of the drums packaged by Uniroyal were clear and legible. Drums are olive green with yellow markings. In general the exterior of the drums selected for sampling did not show any gross signs of deterioration. Six drums showed minor signs of rust around the bottom seam of the drum, four drums showed signs of incidental rust and no rust was observed on the other six drums.

Storage Lids:

All storage lids contained a threaded plexiglass viewing port in order to monitor the liquid level inside the drum. The inside of all drum lids was coated with a protective phenolic coating. Incidental rust deposits were observed in the interior of 14 drum lids, and on two drum lids minor to moderate rust deposits were detected. In general the protective phenolic coating on the storage lids shows good physical properties. There is no evidence of any gross deterioration or flaking off of the protective coating. In all cases the foam rubber gaskets used to seal the lids show good physical properties.

Drum Interior:

The liquid level of the alcohol-water solution inside the storage drums was approximately two to three inches from the top of the drum lip. The interior of all Uniroyal drums was coated with a protective phenolic coating. Incidental rust deposits were observed around the drum lip on all drums examined. On ten drums the phenolic coating did not show any visual signs of deterioration and no rust or scale was observed on the inside of the drums. In six drums incidental rust deposits were detected to a depth of approximately two to four inches. Of this number two drums showed some signs of coating breakdown, that is, the coating was observed to be flaking off at a depth of four to six inches from the drum lip.

Packaging Materials:

No visual signs of deterioration or structural weakness was detected in packaging materials such as Osnaburg drum liners, sawdust, polyethylene bags, duck cloth bags and diaper cloths. However, the black plastic tape used in securing the polyethylene bags showed a definite loss of adhesive properties.

In eight drums the alcohol in contact with the azide showed discoloration varying from pink to red and in six of these drums the diaper cloth and duck cloth bags were stained with a dark reddish colored residue. The alcohol in the other eight drums was colorless.

In all cases the color of the lead azide appeared to be normal (white color).

LEAD AZIDE SAMPLES

Lot Number	Barrel Number	Batch Number	Manufacture Date
JA 4-73	11	539	10/67
JA 4-74	5	880	10/67
JA 4-75	36	589	10/67
JA 4-79	27	429	11/67
JA 4-80	15	710	11/67
JA 4-82	12	1480	11/67
JA 4-83	1	1769	11/67
JA 4-85	28	169	12/67
JA 4-87	17	860	12/67
JA 4-89	12	1610	12/67
JA 4-90	22	109	1/68
JA 4-92	10	790	1/68
JA 4-93	27	1364	1/68
JA 4-94	24	1730	1/68
JA 4-96	12	410	2/68
JA 4-97	1	700	2/68

DRUM EXTERIOR - VISUAL INSPECTION

Lot No.	Barrel No.	Drum Markings	Condition of Drum Exterior
JA 4-73	11	Clear, Legible	No indications of rust around bottom seam
JA 4-74	5	Clear, Legible	Incidental rust around bottom seam
JA 4-75	36	Clear, Legible	No indications of rust around bottom seam
JA 4-79	27	Clear, Legible	No indications of rust around bottom seam
JA 4-80	15	Clear, Legible	No indications of rust around bottom seam
JA 4-82	12	Clear, Legible	No indications of rust around bottom seam
JA 4-83	1	Clear, Legible	Incidental rust around bottom seam
JA 4-85	28	Clear, Legible	Incidental rust around bottom seam
JA 4-87	17	Clear, Legible	No indications of rust around bottom seam
JA 4-89	12	Clear, Legible	Minor rust around bottom seam
JA 4-90	22	Clear, Legible	Minor rust around bottom seam
JA 4-92	10	Clear, Legible	Minor rust around bottom seam
JA 4-93	27	Clear, Legible	Minor rust around bottom seam
JA 4-94	24	Clear, Legible	Incidental rust around bottom seam
JA 4-96	12	Clear, Legible	Minor rust around bottom seam
JA 4-97	1	Clear, Legible	Minor rust around bottom seam

DRUM INTERIOR* - VISUAL INSPECTION

Lot No.	Condition of Storage Lid	Condition of Drum Interior*
JA 4-73	Incidental rust-gasket good	Incidental rust and/or scale depth of 1-2 inches
JA 4-74	Incidental rust-gasket good	Incidental rust and/or scale depth of 1-2 inches
JA 4-75	Incidental rust-gasket good	No indications of rust on drum interior
JA 4-79	Minor rust-gasket good	No indications of rust on drum interior
JA 4-80	Incidental rust-gasket good	No indications of rust on drum interior
JA 4-82	Incidental rust-gasket good	Incidental rust and/or scale depth of 2-3 inches
JA 4-83	Incidental rust-gasket good	Incidental rust and/or scale depth of 1-2 inches
JA 4-85	Incidental rust-gasket good	No indication of rust on drum interior
JA 4-87	Incidental rust-gasket good	No indication of rust on drum interior
JA 4-89	Incidental rust-gasket good	Incidental rust-phenolic coating flaking off
JA 4-90	Incidental rust-gasket good	Incidental rust and/or scale depth of 3-4 inches
JA 4-92	Moderate rust-gasket good	No indications of rust on drum interior
JA 4-93	Incidental rust-gasket good	No indications of rust on drum interior
JA 4-94	Incidental rust-gasket good	No indications of rust on drum interior
JA 4-96	Incidental rust-gasket good	No indications of rust on drum interior
JA 4-97	Incidental rust-gasket good	No indications of rust on drum interior

* The interior of the drum and lid is coated with a protective phenolic coating.

** All drums contained incidental rust deposits around the drum lid.

PACKAGING MATERIALS IN CONTACT WITH DRUM

Lot No.	Color of Alcohol Solution*	Drum Liner**	Sawdust***
JA4-73	Dark Red	Osnaburg, Top sewed, Condition good	Top layer 2-4 inches deep
JA4-74	Dark Red	Osnaburg, Top sewed, Condition good	Top layer 2-4 inches deep
JA4-75	Dark Red	Osnaburg, Top sewed, Condition good	No top layer of sawcust
JA4-79	Dark Red	Osnaburg, Top sewed, Condition good	No top layer of sawcust
JA4-80	Dark Red	Osnaburg, Top sewed, Condition good	No top layer of sawcust
JA4-82	Dark Red	Osnaburg, Top sewed, Condition good	No top layer of sawdust
JA4-83	Dark Red	Osnaburg, Top sewed, Condition good	Top layer 1-2 inches deep
JA4-85	Dark Red	Osnaburg, Top sewed, Condition good	No top layer of sawdust
JA4-87	Dark Red	Osnaburg, Top sewed, Condition good	Top layer 1-2 inches deep
JA4-89	Dark Red	Osnaburg, Top sewed, Condition good	Top layer 1-2 inches deep
JA4-90	Dark Red	Osnaburg, Top sewed, Condition good	Top layer 2-4 inches deep
JA4-92	Dark Red	Osnaburg, Top sewed, Condition good	No top layer of sawdust
JA4-93	Dark Red	Osnaburg, Top sewed, Condition good	No top layer of sawdust
JA4-94	Dark Red	Osnaburg, Top sewed, Condition good	Top layer 2-4 inches deep
JA4-96	Dark Red	Osnaburg, Top sewed, Condition good	Top layer 1-2 inches deep
JA4-97	Dark Red	Osnaburg, Top sewed, Condition good	No top layer of sawdust

*Alcohol-water solutions-liquid level approximately 1 to 3 inches from top of drum lid.

**All drums inspected contained Osnaburg drum liners.

***No top layer of sawdust-packing and/or settling of the sawdust has occurred to the point where there is no longer any top cushioning layer of sawdust.

PACKAGING MATERIALS IN CONTACT WITH LEAD AZIDE*

Lot No.	Color of Alcohol Solution	Condition of Duck Cloth Bag	Condition of Diaper Cloth
JA4-73	Colorless	Good	Good - no stains/residue
JA4-74	Pink/Red	Good	Good - no stains/residue
JA4-75	Colorless	Good	Good - no stains/residue
JA4-79	Pink	Good	Good - no stains/residue
JA4-80	Pink/Red	Good	Good - red colored stains
JA4-82	Pink	Good	Good - red colored stains
JA4-83	Pink	Good	Good - red colored stains
JA4-85	Colorless	Good	Good - no stains/residue
JA4-87	Colorless	Good	Good - no stains/residue
JA4-89	Colorless	Good	Good - no stains/residue
JA4-90	Colorless	Good	Good - no stains/residue
JA4-92	Pink/Red	Good	Good - red colored stains
JA4-93	Colorless	Good	Good - no stains/residue
JA4-94	Pink/Red	Good	Good - red colored stains
JA4-96	Colorless	Good	Good - no stains/residue
JA4-97	Red	Good	Good - red colored stains

COLOR OF LEAD AZIDE

Lot No.	Color of Alcohol in Contact with Drum	Color of Alcohol in Outer Poly Bag	Color of Alcohol in Middle Poly Bag	Color of Alcohol in Inner Poly Bag*	Color of Lead Azide
JA4-73	Red	Red	Colorless	Colorless	White
JA4-74	Red	Red	Red	Pink/Red	White
JA4-75	Red	Red	Pink/Red	Colorless	White
JA4-79	Red	Red	Red	Pink	White
JA4-80	Red	Red	Red	Pink/Red	White
JA4-82	Red	Red	Red	Pink	White
JA4-83	Red	Red	Red	Pink	White
JA4-85	Dark Red	Pink	Colorless	Colorless	White
JA4-87	Dark Red	Red	Colorless	Colorless	White
JA4-89	Dark Red	Colorless	Colorless	Colorless	White
JA4-90	Dark Red	Red	Colorless	Colorless	White
JA4-92	Dark Red	Dark Red	Dark Red	Pink	White
JA4-93	Dark Red	Dark Red	Red	Colorless	White
JA4-94	Dark Red	Dark Red	Dark Red	Pink/Red	White
JA4-96	Dark Red	Dark Red	Dark Red	Colorless	White
JA4-97	Dark Red	Dark Red	Dark Red	Red	White

*This polyethylene bag contained the lead azide.

Appendix H

TRIP REPORT

SPECIAL PURPOSE LEAD AZIDE

SURVEILLANCE STUDIES

Savanna Army Depot
Savanna, Illinois

Joseph R. Smith
July 26-31, 1971

From July 26-31, a representative of the Explosives Division visited Savanna Army Depot, Savanna, Illinois. The purpose of this visit was to obtain samples of Special Purpose Lead Azide in order to continue long term storage surveillance studies. Lead azide stored at Savanna was manufactured and packaged by Dupont during 1967 and 1968.

Mr. J. Lancaster, Director of Surveillance, coordinated this visit and Messrs. Clear, Mills, Martin and Nelson assisted in the sampling of the lead azide. Funding for the sampling operations was provided by Picatinny Arsenal.

Drums from sixteen (16) different lots of Special Purpose Lead Azide were randomly selected for sampling. In addition to sampling the lead azide, the alcohol-water solutions present inside the storage drums were carefully sampled. All samples were shipped to the Explosives Division for testing and evaluation.

During the sampling operation the following observations were noted:

Packaging Configuration:

The DuPont packaged lead azide contained two polyethylene bags one inside the other and each individually sealed with black plastic tape. The lead azide (25 lb batch) is contained in a diaper cloth, with the ends pulled together and tied with cotton cord. Each batch is tagged with a tag showing the batch number. Six batches (150 lbs) of lead azide are packaged in three duck cloth bags each secured with cotton cord (2 batches per bag). The three duck cloth bags are packaged in the innermost polyethylene bag which contains sufficient ethyl alcohol to keep the bags submerged.

Each fifty-five gallon drum is lined with an Osnaburg liner. The bottom of the liner contains 4 to 6 inches of sawdust which acts as a cushioning medium. The polyethylene bags containing the azide is placed on the sawdust cushion and the bag is covered with 4 to 6 inches of sawdust. The top of the liner is sewed in order to keep the packaging configuration together. The drum is then filled with alcohol-water solution to within 1 to 2 inches from the drum lip.

During storage the drum is covered with a storage lid which contains a plexiglass viewing port for monitoring the liquid level inside the drum. The lid contains a foam rubber gasket and is secured to the drum by means of a bolted locking ring.

Drum Exterior:

All markings and/or labeling on the exterior of the drums packaged by DuPont were clear and legible. Drums are white with black markings. In general, the exterior of the drums selected for sampling did not show any gross signs of deterioration. Eleven drums showed minor signs of rust around the bottom seam, of this number three drums also showed signs of minor rust along the side seam of the drums. Two drums showed moderate signs of rust around the bottom seam, in addition both drums also showed signs of minor rust along the side seam of the drums. Three drums showed signs of incidental rust around the bottom seam of the drum.

Storage Lids:

All storage lids contained a plexiglass viewing port in order to monitor the liquid level inside the drums. The plexiglass is secured to the drum lid with sheet metal screws with plastic putty used as a sealant. In most cases leakage was detected around the view port. Twelve of the lids were coated with a protective phenolic coating. Of this number eight lids showed signs of incidental rust and six lids showed signs of minor rust. Two lids did not show any evidence of protective coatings, one of these lids showed signs of moderate rust while the other showed major to severe rusting and scale. In general the lids containing the phenolic coating showed signs of incidental to minor rust while the lids without a protective coating showed signs of moderate to severe rust. In ten cases the gasket used to seal the drum had deteriorated (stretched) to the point where it no longer provided an adequate seal. Six lids contained gaskets which showed good to fair physical properties.

Drum Interiors:

The liquid level of the alcohol-water solution inside the storage drums was approximately one to three inches from the top of the drum lip. The Dupont drums do not show any evidence of a protective coating. On two drums major to severe rusting was observed to a depth of eight to ten inches. Moderate to major rust was observed to a depth of approximately eight inches in two other drums. Five drums showed signs of moderate rust to a depth of six to eight inches, in one case the rust was observed to a depth of eighteen inches. Minor rust was observed in seven drums, the depth of the rust varied from one to eight inches.

Packaging Materials:

No visual signs of deterioration or structural weakness were detected in packaging materials such as Osnaburg drum liners, poly-

ethylene bags, duck cloth bags and diaper cloths. However, the black plastic tape used in securing the polyethylene bags showed a definite loss of adhesive properties.

In fifteen drums the alcohol in contact with the azide was colorless. In one case a pink discoloration was observed. The color of the lead azide was white in all cases.

LEAD AZIDE SAMPLES

Lot Number	Barrel Number	Batch Number	Manufacture Date
Dup 53-18	5	4794	4/67
Dup 53-21	9	5317	4/67
Dup 53-23	17	5737	4/67
Dup 53-25	5	6019	/67
Dup 53-32	2	6729	/67
Dup 53-35	20	7334	/67
Dup 53-38	14	7880	7/67
Dup 53-44	14	8968	8/67
Dup 53-51	14	10103	9/67
Dup 53-73	7	14276	12/67
Dup 53-75	1	14627	1/68
Dup 53-76	14	14971	1/68
Dup 53-77	10	15131	/68
Dup 53-79	4	15466	/68
Dup 53-91	18	1765	5/68
Dup 53-92	17	1955	5/68

DRUM EXTERIOR - VISUAL INSPECTION

Lot No.	Drum Markings*	Condition of Drum Exterior
Dup 53-18	Clear, Legible	Minor rust around bottom seam & along side seam
Dup 53-21	Clear, Legible	Minor rust around bottom seam & along side seam
Dup 53-23	Clear, Legible	Moderate rust around bottom seam & minor rust along side seam
Dup 53-25	Clear, Legible	Moderate rust around bottom seam & minor rust along side seam
Dup 53-32	Clear, Legible	Minor rust around bottom seam
Dup 53-35	Clear, Legible	Minor rust around bottom seam
Dup 53-38	Clear, Legible	Minor rust around bottom seam
Dup 53-44	Clear, Legible	Minor rust around bottom seam
Dup 53-51	Clear, Legible	Minor rust around bottom seam
Dup 53-73	Clear, Legible	Incidental rust around bottom seam
Dup 53-75	Clear, Legible	Incidental rust around bottom seam
Dup 53-76	Clear, Legible	Minor rust around bottom seam
Dup 53-77	Clear, Legible	Minor rust around bottom seam & along side seam
Dup 53-79	Clear, Legible	Minor rust around bottom seam
Dup 53-91	Clear, Legible	Incidental rust around bottom seam
Dup 53-92	Clear, Legible	Minor rust around bottom seam

*Drums are painted white with black markings and labeling

DRUM INTERIOR - VISUAL INSPECTION

Lot No.	Condition of Storage Lid	Condition of Drum Interior*
Dup 53-18	*Incidental rust-gasket good/fair	Minor rust and/or scale depth of 1-2"
Dup 53-21	*Minor rust - gasket deteriorated	Moderate rust and/or scale depth of 6-8"
Dup 53-23	Moderate rust-gasket deteriorated	Moderate/major rust and/or scale depth 8 inches
Dup 53-25	Major rust-gasket deteriorated	Moderate/major rust and/or scale depth 8 inches
Dup 53-32	*Minor rust-gasket deteriorated	Moderate rust and/or scale depth of 6-8"
Dup 53-35	*Minor rust-gasket deteriorated	Major/severe rust and/or scale depth 8 inches
Dup 53-38	*Incidental rust-gasket deteriorated	Major/severe rust and/or scale depth 8-10 inches
Dup 53-44	*Incidental rust-gasket deteriorated	Minor rust and/or scale depth of 4-6"
Dup 53-51	*Minor rust-gasket good/fair	Moderate rust and/or scale depth of 6-8"
Dup 53-73	*Incidental rust-gasket good	Minor rust and/or scale depth of 2-4"
Dup 53-75	*Incidental rust-gasket good	Moderate rust and/or scale depth of 6-8"
Dup 53-76	*Incidental rust-gasket good	Minor rust and/or scale depth of 4-6"
Dup 53-77	*Minor rust-gasket deteriorated	Moderate rust and/or scale depth of 18"
Dup 53-79	*Minor rust-gasket good/fair	Minor rust and/or scale depth of 6-8"
Dup 53-91	*Incidental rust-gasket deteriorated	Minor rust and/or scale depth of 4-6"
Dup 53-92	*Incidental rust-gasket deteriorated	Minor rust and/or scale depth of 2-4"

*Drum lid containing a protective phenolic coating.
**Drum interiors do not show any evidence of a protective coating. Below the depths indicated the interior of the drums was smooth and shiny.

PACKAGING MATERIALS IN CONTACT WITH DRUM

Lot No.	Color of Alcohol Solution*	Drum Liner**	Sawdust
Dup 53-18	Black	Osnaburg-top sewed-condition good	Bright color, top layer 4-6" deep
Dup 53-21	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-23	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-25	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-32	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-35	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-38	Black	Osnaburg-top sewed-condition good	Black color, top layer 4-6" deep
Dup 53-44	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-51	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-73	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-75	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-76	Red	Osnaburg-top sewed-condition good	Bright color, top layer 4-6" deep
Dup 53-77	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-79	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-91	Black	Osnaburg-top sewed-condition good	Black color, top layer 2-4" deep
Dup 53-92	Black	Osnaburg-top sewed-condition	Black color, top layer 4-6" deep

*Alcohol Solution - Liquid level approximately 1 to 3 inches from top of drum lip
**All Osnaburg drum liners were stained black.

PACKAGING MATERIALS IN CONTACT WITH LEAD AZIDE

Lot No.	Color of Alcohol Solution	Condition of Duck Cloth Bag	Condition of Diaper Cloth
Dup 53-18	Colorless	Good	Good-no stains/residue
Dup 53-21	Colorless	Good	Good-no stains/residue
Dup 53-23	Colorless	Good	Good-no stains/residue
Dup 53-25	Colorless	Good	Good-no stains/residue
Dup 53-32	*Colorless	Good	Good-no stains/residue
Dup 53-35	Colorless	Good	Good-no stains/residue
Dup 53-44	Colorless	Good	Good-no stains/residue
Dup 53-51	Colorless	Good	Good-no stains/residue
Dup 53-73	Colorless	Good	Good-no stains/residue
Dup 53-75	Colorless	Good	Good-no stains/residue
Dup 53-76	Colorless	Good	Good-no stains/residue
Dup 53-77	Pink	Good	Good-no stains/residue
Dup 53-79	Colorless	Good	Good-no stains/residue
Dup 53-91	Colorless	Good	Good-no stains/residue
Dup 53-92	Colorless	Good	Good-no stains/residue

*This barrel was opened on 15 December 1970 and a 15 pound batch of lead azide was removed and shipped to Lone Star Army Ammunition Plant.

COLOR OF LEAD AZIDE

Lot No.	Color of Alcohol Solution in Contact with Drum	Color of Alcohol Solution in Outer Polyethylene Bag	Color of Alcohol Solution in Inner Polyethylene Bag*	Color of Lead Azide
Dup 53-18	Black	Black	Colorless	White
Dup 53-21	Black	Black	Colorless	White
Dup 53-23	Black	Red/Brown	Colorless	White
Dup 53-25	Black	Red/Brown	Colorless	White
Dup 53-32	Black	Pink/Red	Colorless	White
Dup 53-35	Black	Black	Colorless	White
Dup 53-38	Black	Black	Colorless	White
Dup 53-44	Black	Dark Red	Colorless	White
Dup 53-51	Black	Black	Colorless	White
Dup 53-73	Black	Black	Colorless	White
Dup 53-75	Black	Colorless	Colorless	White
Dup 53-76	Red	Red	Colorless	White
Dup 53-77	Black	Black	Pink	White
Dup 53-79	Black	Pink	Colorless	White
Dup 53-91	Black	Pink	Colorless	White
Dup 53-92	Black	Colorless	Colorless	White

*This polyethylene bag contained the lead azide.

Appendix I

A STUDY OF THE EFFECTS OF LONG TERM STORAGE (WET) ON SPECIAL PURPOSE LEAD AZIDE

Explosives Division
10 December 1969
Arthur C. Forsyth
Joseph R. Smith
David S. Downs
Harry D. Fair, Jr.

INTRODUCTION

Preliminary reports on this task have been submitted describing the results of inspections of storage facilities (particularly the interior conditions of storage drums) both at Savanna Ordnance Depot and Ravenna Army Ammunition Plant. In addition, a report presenting an analytical study and evaluation of packaging materials and storage media (50/50 EtOH/H_2O) used for Special Purpose Lead Azide (SPLA) storage was submitted 18 August 1969. They indicated that considerable deterioration of the packaging material had taken place and that physical and chemical changes may possibly have occurred in the packaging materials and in the lead azide.

It is the purpose of this report to present data on the properties of seven samples of lead azide which have been subjected to one summer temperature cycle and to compare these results with those obtained from the original samples as received from the storage facilities.

RESULTS AND DISCUSSION

Thirty-three lead azide samples (27 SPLA and 6 RD 1333) have been received from the storage depots and repackaged in polyethylene bottles under 50/50 EtOH/H_2O, each bottle containing the amount of azide to be used for one periodic test. The temperature cycling program was scheduled to begin upon receipt of the lead azide samples, but this part of the program has been considerably delayed due to impedence in purchasing and subsequent manufacture of a suitable temperature cycling cabinet. The cabinet was finally delivered November 3rd by Tenney Engineering Inc. and is being held in stores pending funding of the Lead Azide storage study.

The unavailability of the temperature cycling cabinet or use of other suitable cycling facilities necessitated placing these samples in an explosives storage house. It was determined that the variation in temperature in this storage facility is not significantly different from that encountered by the lead azide stored at the Savanna and Ravenna Depots; if anything, the temperature differentials are probably less drastic at Picatinny. Data was therefore obtained on seven samples subjected to this first summer temperature cycle and is compared to that obtained from the original 33 samples.

Photomicrographs

Photomicrographs (P.M.G.'s) were taken of the 33 original samples immediately upon receipt. The following procedure was used: five microscope slides were prepared containing randomly selected portions of the sample. These slides were scanned rapidly and the most representative slide selected for closer study. However, if any irregularities were observed they were noted and that slide was also held for further investigation. The selected slides were then closely scrutinized and at least two areas of the slide were photographed. Also, any irregularities such as crystals that were not immediately identifiable were photographed. The P.M.G.'s of all samples were compared with P.M.G.'s of laboratory batches of R.D. 1333 and of freshly prepared SPLA. Photomicrographs of irregular crystals were compared with P.M.G.'s of crystalline lead azide and sodium carboxymethylcellulose in crystalline form since some doubt exists as to whether it appears as a gelatinous or crystalline material during production processes.

The P.M.G.'s obtained after the first cycle were produced in an identical manner to those taken upon receipt of the storage samples. It can be seen in Figures 1, 2, 3 that most samples after this first temperature cycle show the appearance of small, clear crystals, the

most predominant of these being OLM-67-5, DUP 53-44, DUP 53-17 and JA4-84. Although only one RD 1333 sample was tested, it is of interest to note the growth of crystals from, and remaining attached to, the original particles (Figure 11, page 29).

Impact Testing

The program for periodic testing required that impact tests be conducted on 15 "as received" samples and that after each cycling period 6 samples be withdrawn and tested. However, it became obvious that the arrival time of the cycling equipment ordered for this investigation was completely unpredictable, so it was considered necessary to obtain the impact sensitivity of the entire 33 samples when received.

All impact data was computer analyzed using the methods developed by this Division for "Gravel Mine" studies.* This method compares the sample data to a standard, and sensitivity changes are evaluated when deviations from the standard occur. Also, it readily allows for the comparison of any individual samples with another. In this case, where all of the samples were tested when received, the subsequent tests will be individually compared to the "as received" data. A standard was also tested for reference purposes.

As mentioned previously, samples have been withdrawn from storage and tested as "first cycle" samples. One RD1333 and six SPLA samples were impact tested. The mean critical heights (50% hgts) and standard deviations for these samples "as received" and for "1st cycle" are given in Table 1. Two factors are considered to be significant for these results: (1) the fact that all samples show an increase in sensitivity no matter how small, (2) three of seven samples have a sensitivity increase considered to be significant. The largest change in 50% height observed was 3.5 inch (OM 2-2). This represents a real change since it is much larger than the error limit of the experiments as indicated by the standard deviation in Table 1. Since the 50% height of the "as received" sample was 9 inches, the 3.5 inch change in 50% height represents a change by one third.

A thorough search of the photomicrographs of sample OM 2-2 (RD1333) revealed no small individual crystals as in the SPLA samples but did show small crystallites growing or extending from the original particles (Figure 11, page 29).

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* P.J. Kemmey, Picatinny Arsenal TM 1812, April 1968.

Differential Thermal Analysis (DTA)

This technique has been under consideration for utilization as a criterion of sensitivity for a period of time. However, it was observed early in this study that when using the existing techniques the final decomposition products of the lead azide were various oxides of lead instead of metallic lead. This gives rise to different decomposition curves which are dependent upon experimental conditions, such as heating rate, etc. It was originally planned to use the data accumulated during this study in an attempt to correlate impact sensitivity with DTA data. It was hoped that with the volume of data accumulated during this study a reliable statistical evaluation could be obtained relating these two types of measurements.

Some time was therefore devoted to the development of what was considered to be a satisfactory method of DTA analysis of lead azide. Modifications of the DTA sample cell were made so that the analysis could be performed with the sample in an inert gaseous environment. The present procedure consists of evacuating the DTA sample compartment with a diffusion-pumped vacuum system (approx. 10^{-6} torr) followed by back filling with helium gas. This procedure results in complete decomposition of the lead azide to metallic lead. In addition it is possible to obtain complete decomposition traces without the occurrence of detonation (Figure 7).

For convenience, the individual traces are not presented in this report, but rather the temperature at which the peak reaction exotherm temperature occurs are given in Table 2 for the samples analyzed to date. The temperature of onset of the exothermic reaction is, of course, an extremely important parameter. We are, at present, not as satisfied with the introductory portion of our exotherm traces as with peak temperatures. This dissatisfaction results mostly from minor problems with base line stability which, in our opinion, need further investigation before we can positively pinpoint the onset of the reaction. The investigation of this portion of the trace will be continued by this Division.

Electron Paramagnetic Resonance (EPR)

A basic research study of the effects produced by the incorporation of dopants in the crystal lattice of azides (primarily lead azide) is being conducted by the Solid State Branch of this Division. EPR techniques are used to identify the dopants and to establish their position in the host crystal lattice. The coloration (reddish) of some of the SPLA samples strongly suggested the presence of $Fe(N_3)^{++}$ ions in the crystal lattice. The knowledge accumulated from the basic study was used to identify the dopants present in the SPLA.

The red coloration found in production lead azide is not unfamiliar and is generally the result of $Fe(N_3)^{++}$ ions in the lead azide lattice. The source of $Fe(N_3)^{++}$ can usually be traced to impurities in the sodium azide starting material. Since there is some indication that the presence of these iron impurities changes the sensitivity of lead azide, "red" batches are no longer acceptable for production loading purposes. All of the storage samples investigated here gave a characteristic $Fe(N_3)^{++}$ paramagnetic absorption at an approximate field strength of 1600 gauss and a frequency of 9.2 Kmc. This absorption occurs when an $Fe(N_3)^{++}$ ion is incorporated at an asymmetrical lattice site as in the case of lead azide. The iron absorption peaks observed here were relatively weak except in the case of Olin Mathieson samples where they were 4 to 5 times larger than those obtained for DuPont or Joliet Arsenal samples. As stated in a previous report, it is believed that the difference of permeability of inner packaging materials easily explains the variations in amounts of iron present. The effects of permeability were further demonstrated when Mn^{++} and $Fe(N_3)^{++}$ were shown by EPR measurements to be present in samples taken from inner packaging materials.

The broad paramagnetic absorption that spans the entire spectrum (Figures 4, 5 and 6) is of interest but has not yet been satisfactorily explained. It does not appear in samples of pure lead azide prepared in the laboratory and is believed to be caused by basic lead azide that is formed from the hydrolysis of lead azide. However, another possibility is that this absorption may be caused by the presence of lead carbonate. Samples of lead azide containing varying amounts of basic lead azide were prepared in the laboratory and the EPR spectra obtained. The broad paramagnetic absorption peak was present and its intensity was found to increase with increasing basicity of the sample.

It was demonstrated from the EPR data that the intensity of the broad peak in the absorption spectra of the production samples is greater for the samples packaged in polyethylene i.e. JA 4-57 and DUP 53-79. This is consistent with the hydrolysis of lead azide occurring more easily inside the less permeable polyethylene bags than in the permeable Olin Mathieson containers since impurities, particularly metal cations, can easily interfere with the reaction. EPR spectra have not as yet been obtained for the 1st cycle samples.

SUMMARY

It would be foolish to draw many definite conclusions from a surveillance study after only one season (cycle). However, since this program has been prematurely terminated it is worthwhile to assess what positive information has been obtained and to indicate data which points out reasons for present or future concern.

The appearance of transparent crystals in the majority of the "1st cycle" samples certainly indicates that in an isolated lead azide-$EtOH/H_2O$ system at ambient conditions recrystallization of the lead azide can occur at a significant rate. The morphology of the crystals indicates that they are probably the α-modification of lead azide. Continued formation of new crystals or added growth to those already formed would certainly create an undesirable situation.

The Impact Sensitivity results indicate a shift toward increased sensitivity after the one temperature cycle. For four of the samples tested the 50% height decreased approximately 1 inch. This might not be significant except for the fact that it occurred after only one cycle. However, three of the samples have changes in sensitivity (50% heights) which are considered to be extremely significant. The sensitization of these samples is most probably the result of the formation of crystalline alpha lead azide brought about by a cyclic solvation and reprecipitation of the lead azide. These results, although in no way conclusive, certainly indicate some need for concern.

The results obtained from the DTA studies to date show no significant changes in the peak temperatures. Fe^{+3} and Mn^{+2} impurities have clearly been observed in the crystal lattice of the lead azide by EPR. This can only arise from recrystallization of the lead azide in the presence of Mn and Fe impurities in the storage solution or in the initial manufacturing process. Since both Mn and Fe are observed (the principal components of the steel drum) it is believed that these impurities are introduced by recrystallization in storage. Unfortunately, the manufacturers batch surveillance samples have been destroyed.

TABLE 1

Impact Testing

SAMPLE	MEAN CRITICAL HGT (50% Hgt)		STANDARD DEV	
	"As Received"	1st Cycle	"As Received"	1st Cycle
JA4-84	9.60	8.70	2.421	1.725
JA4-52	8.70	7.50	1.605	2.004
DUP53-44	9.50	7.30	2.004	1.943
DUP53-17	9.80	6.80	2.330	1.424
OM 67-5	6.70	5.70	2.485	2.134
OM 66-25	8.40	7.70	1.705	1.943
OM 2-2	9.00	5.50	1.291	1.902

TABLE 2

DTA

Peak Temperature of Exotherm °C

SAMPLE	AS RECEIVED	AFTER 1st CYCLE
OM 2-2	det(1) 313(2)	det 313
JA 4-52	det 313	det 314
OM 67-5	313	314
OM 66-25	317	det 313
JA 4-84	314	det 314
DUP 53-17	313	314
DUP 53-44	313	det 314

(1) All detonations are reported.

(2) Duplicates were run on all samples reported and were precise to ±1°C.

JA-4-84
As Received

JA-4-84
1st Cycle

DUP 53-44
As Received

DUP 53-44
1st Cycle

JA4-52
As Received

JA-4-52
1st Cycle

DUP 53-17
As Received

DUP53-17
1st Cycle

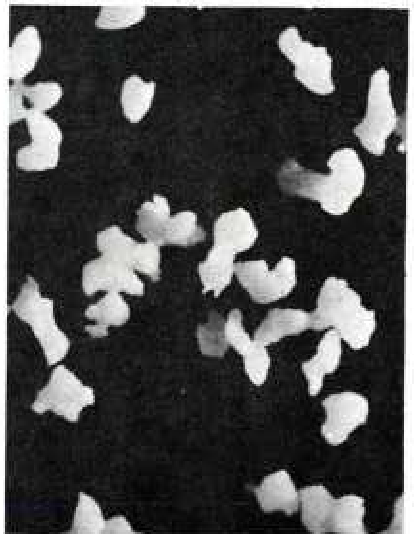
Photomicrographs SPLA as Received & 1st Cycle
FIGURE 1

SPLA OM 67-5
As Received

SPLA OM 67-5
1st Cycle

RD 1333 OM 2-2
As Received

RD 1333 OM 2-2
1st Cycle



SPLA OM 66-25
As Received

SPLA OM 66-25
1st Cycle

Photomicrographs SPLA & RD 1333 As Received & 1st Cycle

FIGURE 2

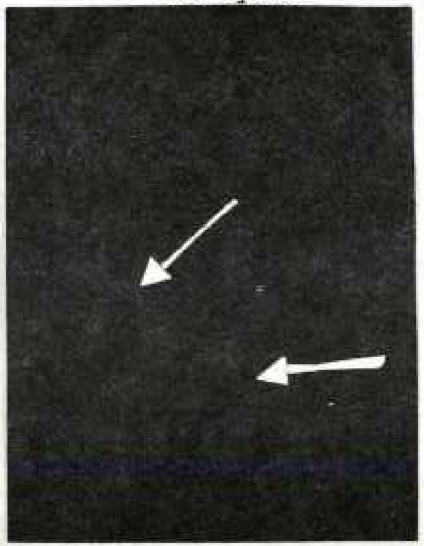
SPLA DUP 53-17
1st Cycle

SPLA DUP 53-44
1st Cycle

SPLA JA 4-84
1st Cycle

SPLA OM 67-5
1st Cycle

RD 1333 OM 2-2
1st Cycle



SPLA DUP 53-44
1st Cycle

Sodium Carboxy-
Methyl Cellulose

Lead Azide
Laboratory Preparation

Photomicrographs of Crystals Found in 1st Cycle Samples,
Also Sodium CMC And A Laboratory Sample P_bN_6
FIGURE 3

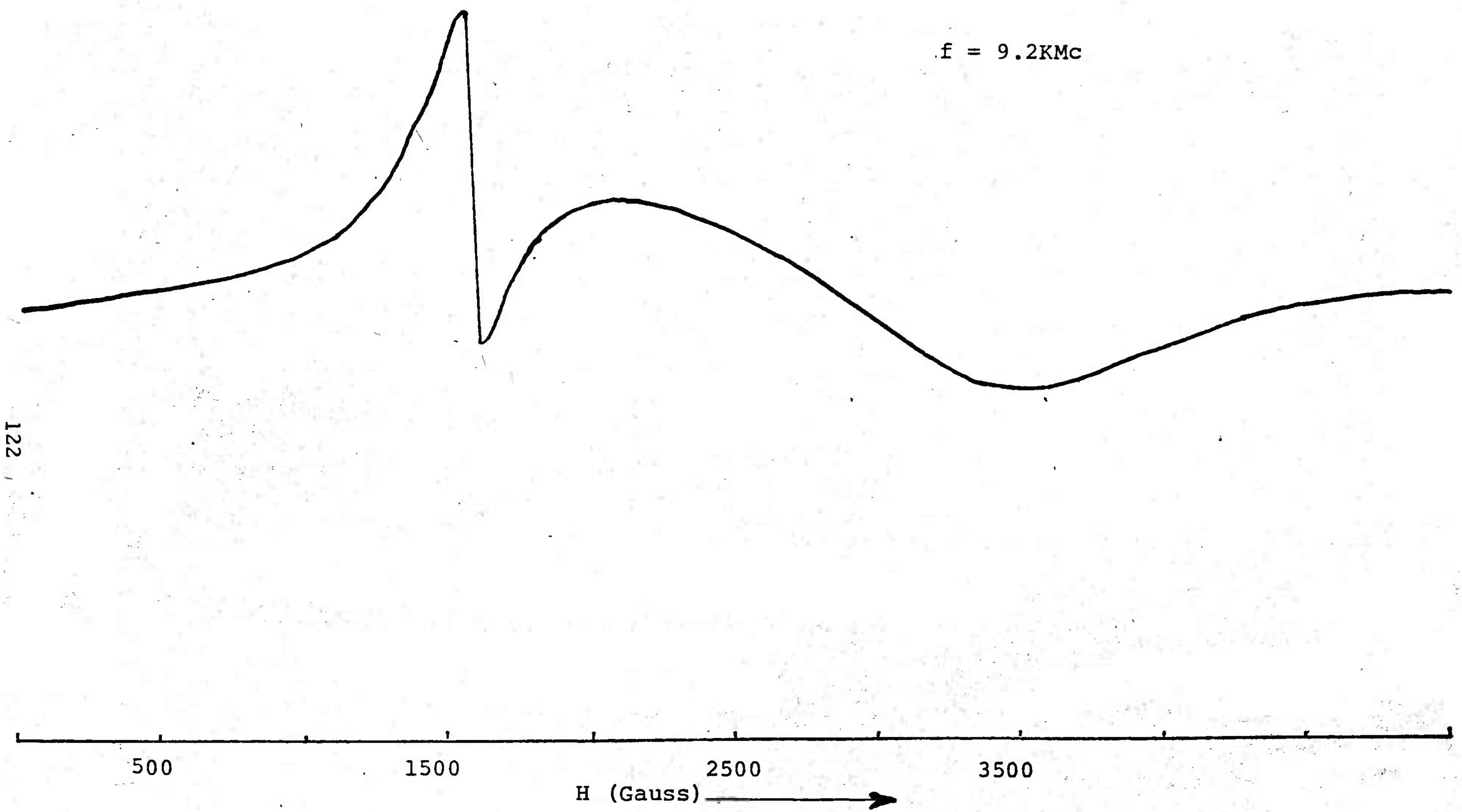


Fig 4 Electron Paramagnetic Resonance Spectra SPLA OM 1-20 as Received

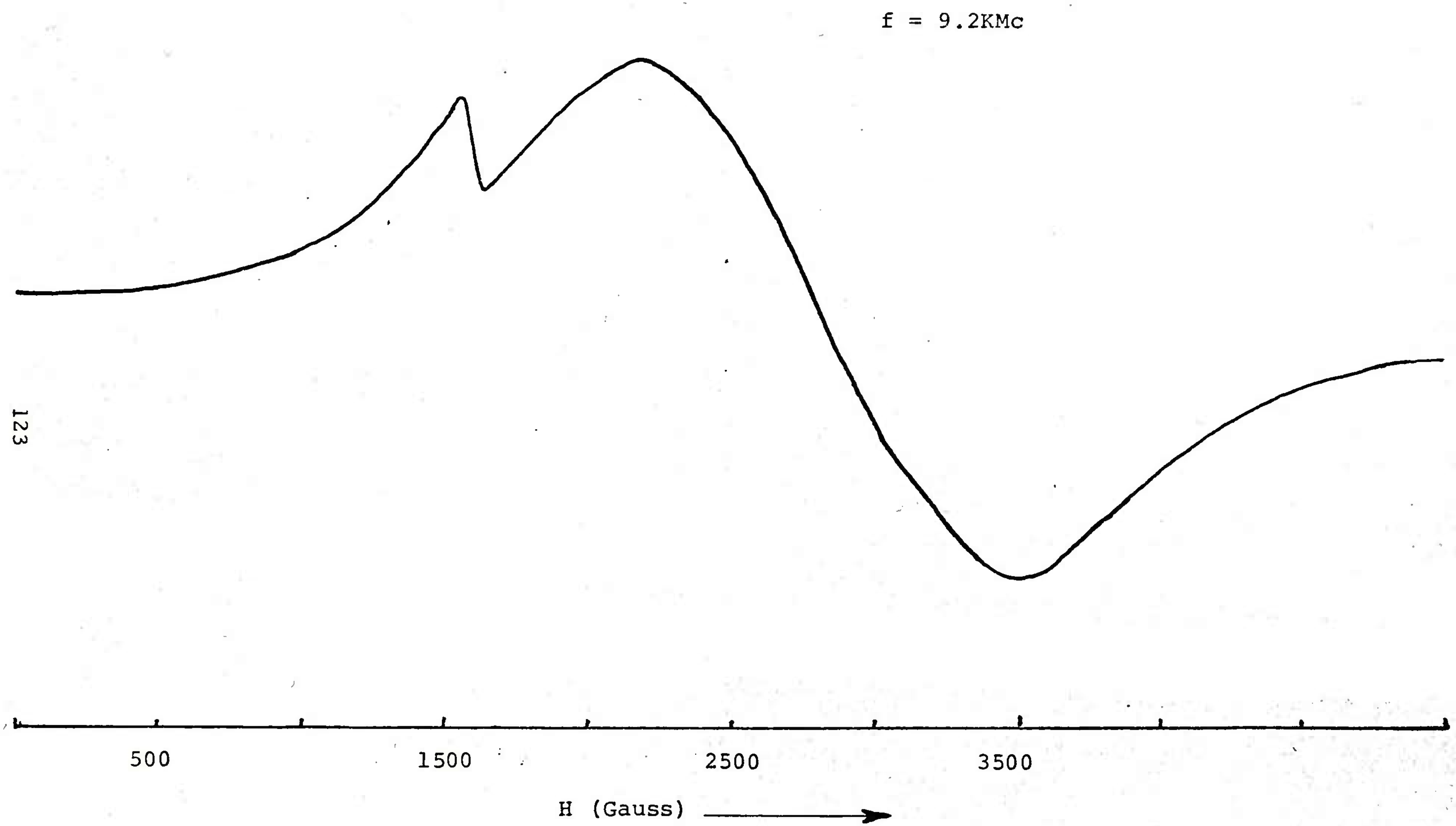


Fig 5 ELECTRON PARAMAGNETIC RESONANCE SPECTRA SPLA JA 4-57 AS RECEIVED

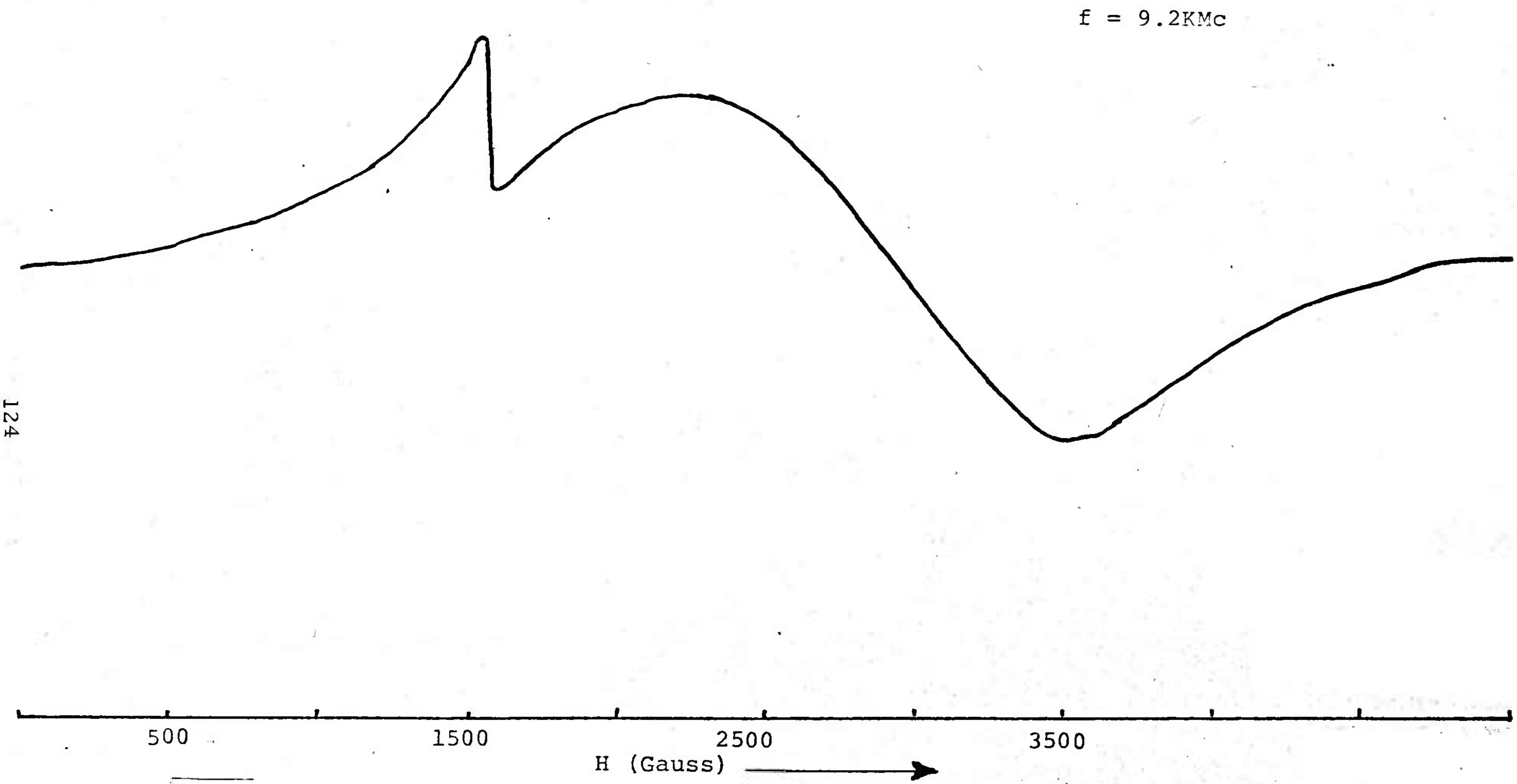


Fig 6 ELECTRON PARAMAGNETIC RESONANCE SPECTRA SPLA DUP 53-79 AS RECEIVED

SAMPLE: Lead Azide 1st Cycle	SIZE 0.50 mg/2 mm tube	ATM. Helium - 900 cc/min.	RUN NO.
	REF. glass	SCALE SETTING T 50 °C/IN. $\triangle$ T 0.2 °C/IN.	DATE 11/3/69
	PROGRAM MODE		OPERATOR
ORIGIN: SPLA JA-4-84	RATE 10 °C/MIN, START °C		

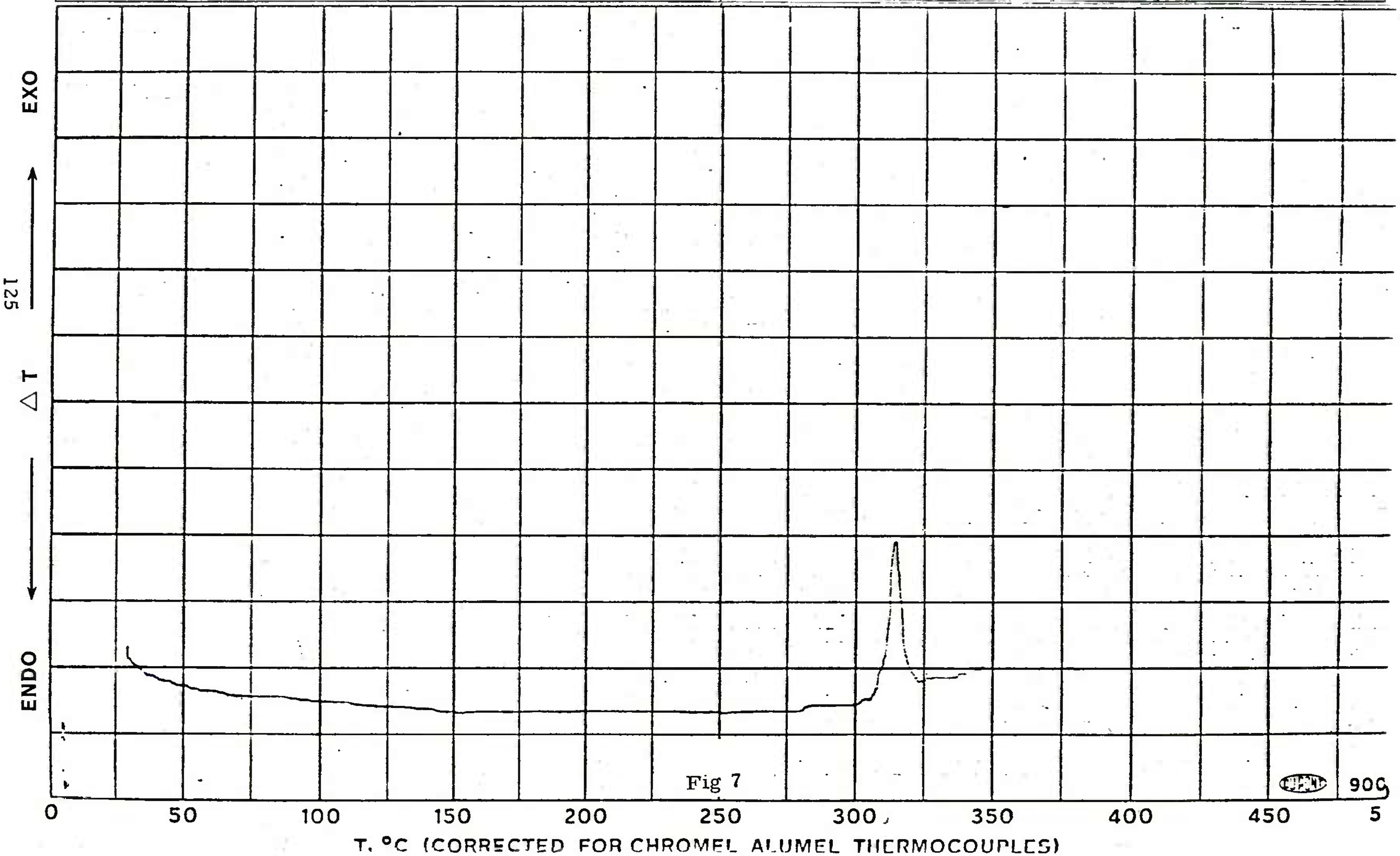


Fig 7

Appendix J

Ball Drop Impact Tests

RD-1333 Lot Dup 51-76

Batch	50% Fire Height (Inches)	Std. Dev.
3785	20.0	3.9
3786	19.4	3.6
3787	20.0	
3788	20.8	4.8
3789	20.2	3.5
3790	20.2	3.3
3791	20.6	2.4
3792	20.7	3.3
3793	20.1	2.7
3794	20.5	3.8

Appendix K

SUBJECT: PA Impact vs Ball Drop Sensitivity

18 February 1971
Mr. Carrigan/ga/5404

1. It is stated that the 8.35 gm Ball Drop Test is far less expensive than the 2 kg PA Impact Test.

2. Graphic review of "least square" curves reflecting each test type reveals the PA test to have less absolute variation (smaller standard deviation) than the Ball Drop Test but the Ball Drop Test to have less relative variation (standard deviation as percent of mean value).

3. This finding suggests that the Ball Drop Test may be a more precise evaluation of sensitivity than the PA Impact Test, as shown by its calculated coefficient of variation (relative standard deviation). Also, the possible impreciseness of the PA Impact Test may account for any insensitivity to differences among lots.

4. The values utilized for the foregoing comment are as follows:

MFG	TEST	$\overline{X}$	S	C of V
Olin-Math	PA	9.717	1.974	.203
	BALL	24.283	3.524	.145
DuPont	PA	9.783	1.795	.183
	BALL	21.383	2.906	.136
Uniroyal	PA	9.283	1.382	.149
	BALL	21.800	2.996	.137

AUGUSTUS STANFIELD
Ch, Math. & Stat. Br.
ADD., QAD

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13. ABSTRACT

Data obtained by the Explosives Division, FRL, Picatinny Arsenal, in the course of a surveillance study of stored special purpose lead azide, are presented. Two separate investigations are being reported: (1) a completed temperature cycle study; and (2) a continuing surveillance program that is concerned with the condition of the stored special purpose lead azide, and the storage containers. Included in the report are results of mechanical sensitivity tests, differential thermal analyses, microscopic surveys, and assay analyses. Relevant trip reports and laboratory studies are included as appendices.

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14. KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
Special purpose lead azide (SPLA)						
Long term storage of SPLA						
Surveillance of stored SPLA						
Compatibility of SPLA with storage container						
Electron paramagnetic resonance spectra of SPLA indicating Fe cation inclusion into crystal lattice						
Packaging configuration of SPLA storage samples						
Differential thermal analysis of SPLA						
Chemical analysis of SPLA and the storage medium						
Inspection of SPLA at various storage installations						
Temperature cycle study of SPLA						
Mechanical sensitivity of SPLA						
Ball drop impact test of SPLA						
Microscopic study of SPLA						